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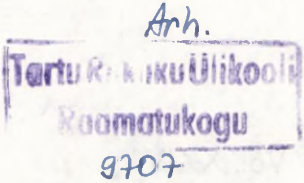


Organic Reactivity
Vol. 24 2(86) 1987

REACTIVITY OF DERIVATIVES OF PHENYLANTHRANILIC ACID II. KINETICS OF ALKALINE HYDROLYSIS REACTION OF METHYL ESTER DERIVATIVES OF 4-NITRO-N-PHENYLANTHRANILIC ACID IN BINARY DIOXANE-WATER SOLVENT

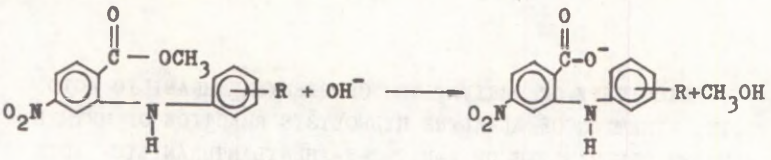
A.N. Gaidukevich, E.N. Svechnikova, and G. Sim
Kharkov State Pharmaceutical Institute, Kharkov,
the Ukrainian S.S.R.

Received July 28, 1987.

The kinetics of alkaline hydrolysis reaction of 9 methyl ester derivatives of 4-nitro-N-phenylanthranilic acid has been studied in the binary dioxane-water solvent (at 60 volume % of dioxane) in temperature range 45-85°C. The bimolecular constants of the reaction rate were also determined. The thermodynamic activation parameters have been calculated. It has been established that the reaction series studied obeys the Hammett equation, although the 2'- and 4'-derivatives can be described by different equations. It has been shown that there is isokinetic correspondence with the ethalpic control type.

In order to continue our studies[1] concerning the reactivity of the derivatives of phenylanthranilic acids, being promising pharmacophores, the alkaline hydrolysis of methyl ester derivatives of 4-nitro-N-phenyl anthranilic acid has been studied in the binary dioxane-water solvent (at 60 vol-

ume % of dioxane) in temperature range 45-85°C:



The reaction rate constants were determined according to the change of nucleophilic (OH^-) concentration in time. The methods of kinetic measurements are similar to those applied in[1]. The reaction studied obeys the second order kinetic equation:

$$\frac{dx}{dt} = k \cdot (a-x) \cdot (b-x) \qquad (1)$$

where a and b denote the initial concentrations of the ester and alkali, respectively in mol/l; x is the current concentration of the reaction product (mol/l) at time moment t (s); k (l/mol·s) is the reaction rate constant. Interrogation of Eq. (1) yields the second order rate constant:

$$k = \frac{2.303}{t \cdot (b-a)} \cdot \log \frac{a \cdot (b-x)}{b \cdot (a-x)} \qquad (2)$$

The k value is corrected, taking into consideration the volumetric extension of the solvent caused by the temperature change from 25°C to 0°C, multiplying by the d_{25}/d_t factor, where d_{25}, d_t denote the density of the solvent at temperatures 25°C and t°C.

The reaction rate constants calculated according to Eq. (2), corrected by the solvent's volumetric extension at different time moments, have stable values not exceeding the limits of the experiment. Consequently, the reaction in total has the second order, as to the nucleophile and substrate the first order.

The rate constants of the reaction series studied are

Table 1

Rate Constants of Alkaline Hydrolysis Reaction of Methyl Ester Derivatives of 4-Nitro-N-Phenylanthranilic Acid at Various Temperatures

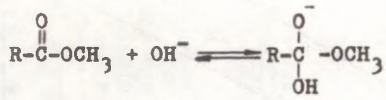
R	$k \cdot 10^3$, $l \cdot mol^{-1}$ s^{-1} at T,K				
	318 K	328 K	338 K	348 K	358 K
H	1.70±0.10	3.24±0.12	5.89±0.03	9.33±0.11	13.8±0.14
4'-CH_3	1.20±0.07	1.99±0.08	3.98±0.05	6.17±0.07	9.77±0.11
3',5'-CH_3	1.38±0.06	2.52±0.07	3.98±0.08	7.08±0.07	10.5±0.12
3',4'-CH_3	0.93±0.04	1.82±0.08	3.16±0.08	5.25±0.08	8.51±0.09
4'-OCH_3	0.93±0.04	1.74±0.04	2.82±0.06	5.25±0.12	7.94±0.07
4'-Cl	3.31±0.11	5.62±0.09	10.0±0.12	14.13±0.03	21.91±0.09
2'-CH_3	0.89±0.05	1.60±0.06	2.61±0.09	4.38±0.06	6.93±0.08
2'-OCH_3	0.72±0.03	1.24±0.03	2.27±0.04	3.73±0.03	6.00±0.04
2'-Cl	2.30±0.12	3.80±0.06	6.22±0.07	9.70±0.08	14.8 ±0.11

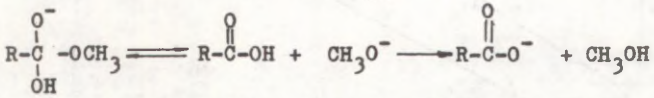
Table 2

Parameters of the Hammett Equation for Alkaline Hydrolysis Reaction of Methyl Ester Derivatives of 4-Nitro-N-Phenylanthranilic Acid at Various Temperatures

	3'-, 4' - substituents					2'- substituents			
T,K	ρ	log k_o	r	S	T,K	ρ	log k_o	r	S
318	1.110±0.017	-2.739±0.034	0.9935	0.026	318	1.062±0.011	-2.862±0.024	0.9971	0.009
328	1.046±0.016	-2.487±0.032	0.9937	0.024	328	1.011±0.010	-2.631±0.023	0.9971	0.009
338	0.985±0.012	-2.252±0.024	0.9960	0.018	338	0.938±0.024	-2.406±0.059	0.9978	0.022
348	0.902±0.12	-2.045±0.023	0.9955	0.018	348	0.880±0.015	-2.200±0.033	0.9922	0.012
358	0.884±0.14	-1.860±0.027	0.9974	0.020	358	0.833±0.016	-2.010±0.036	0.9915	0.014

determined by the substituents' nature and position in the non-anthranilic fragment of the molecule (Table 1). Increase of the donor character of the substituents decelerates the rate of the alkaline hydrolysis at all temperatures studied. Taking into account this effect, the following mechanism of alkaline hydrolysis[2] can be suggested for reaction series $B_{AC}2$:





It should be mentioned that the esters with 2'-substituents in the molecule have the slowest hydrolysis rate in comparison with 4'- and 3'- substituents.

The substituent effect on the reactivity of esters was quantitatively assessed by means of the Hammett equation:

$$\log k = \log k_o + \rho \cdot \sigma \qquad (3)$$

It follows from the data of Table 2 that the reaction series studied obeys the Hammett equation, the correlation coefficient value being comparatively high. Nevertheless, it is not possible to describe the effect of both the 3'- and 4'-, as well as the 2'- substituents using a single equation, since in case of the 2'- substituents the corresponding straight line is situated somewhat lower than that in case of the 3'- and 4'- substituents, at all temperatures studied (Fig. 1). The positive ρ value once again proves the $B_{AC}2$- type hydrolysis mechanism of this reaction series. The susceptibility of the electron system of 4-nitro-N-phenyl-anthranilic acid to the substituent effect is quite insignificant in comparison with that of the substituted benzoic acids (ρ=2.26 was calculated according to the data of[3]). It can be explained by the fact that the substituents are situated rather far from the reaction center in a non-anthranilic fragment. The ρ values are quite close for

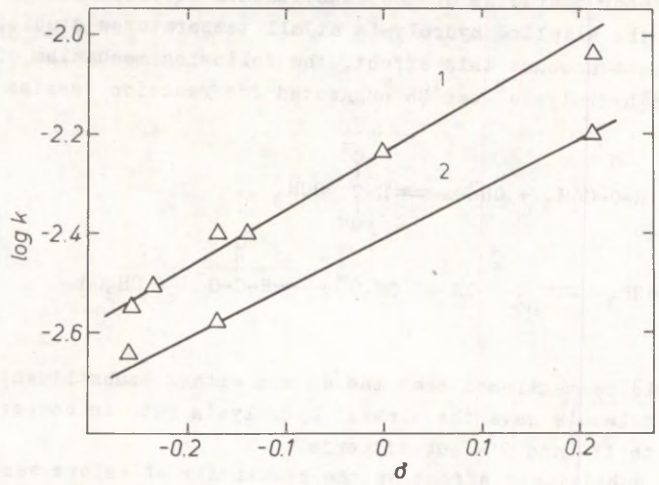


Fig. 1. Dependence log k - f(σ) at 338K for 3'-, 4'-(1) and 2'-(2)- substituents in a methyl ester molecule of 4-nitro-N-phenylanthranilic acid.

3'-, 4'- and 2'- substituents and only slightly differ from the ρ alkaline hydrolysis of the 4'- derivatives of β-dimethyl-aminoethyl ester of 4-chlore-N-phenyl-anthranilic acid; consequently, the mechanisms of transferring electronic effects of substituents are similar in these cases. The ρ value is dropping with the increase of the temperature.

The reaction rate constants obey the Arrhenius equation:

$$\ln k = \ln A - \frac{E_A}{RT} \qquad (4)$$

It enabled us to calculate the activation energy (E_A) and the pre-exponential factor (ln A) values (Table 3). The donor substituents bring about the increase of the activation energy (the 3',5'-CH_3 substituent is excluded) while the acceptor substituents have the contrary effect. The 2'- substituents have a remarkably amaller E_A value than the 4'- substituents. The correlation between the activation parameters (E_A and ln A) and the σ-constants was studied. The activation energy for the 3'- and 4'- substituents can be described as:

$$E_A = (47.9\pm1.8) - (12.4\pm0.9) \cdot \sigma \qquad (5)$$

$$n=5 \quad S=1.4 \quad r=0.9924$$

Table 3

Kinetic Activation Parameters (E_A and ln A) of Alkaline Hydrolysis Reaction of Methyl Ester Derivatives of 4-Nitro-N-Phenylanthranilic Acid.

R	E_A kJ/mol	ln A	r	S
H	49.8±0.6	12.5±1.4	0.9976	0.067
4'-CH_3	49.4±0.6	12.0±1.0	0.9972	0.072
3',5'-CH_3	48.2±0.4	11.7±0.8	0.9989	0.042
3',4'-CH_3	52.0±0.3	12.7±0.9	0.9959	0.032
4'-OCH_3	51.0±0.4	12.3±1.4	0.9989	0.046
4'-Cl	44.6±0.4	11.2±0.6	0.9980	0.054
2'-CH_3	48.4±0.1	11.3±0.5	0.9989	0.015
2'-OCH_3	50.5±0.2	11.8±0.8	0.9969	0.027
2'-Cl	44.1±0.6	10.6±0.2	0.9961	0.071

A small number of the 2'-substituents does not permit to reach a statistically reliable correlation dependence E_A-f(σ). The ln A values for different substituents are quite close but the statistically reliable linear correlation dependence ln A-f(σ) is not observed (r=0.673).

The thermodynamic activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) calculated according to the Eyring equation[4] and the second

Table 4

Thermodynamic Activation Parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}_{318}$) of Alkaline Hydrolysis Reaction of Methyl Ester Derivatives of 4-Nitro-N-Phenylanthranilic Acid.

R	$\Delta G^{\neq}$ kJ/mole					$\Delta H^{\neq}$	$\Delta S^{\neq}$	r	S	$T\Delta S$ kJ/mole
	318 K	328 K	338 K	348 K	358 K	kJ/mole	J/degree			318 K
H	94.8	96.3	97.8	99.3	100.8	47.0±0.6	-150.3±2.0	0.9971	0.068	-47.8
4'-CH_3	95.8	97.4	98.9	100.4	101.9	47.6±0.5	-151.7±1.9	0.9977	0.062	-48.2
3',5'-CH_3	95.4	97.0	98.6	100.1	101.7	45.4±0.4	-157.3±1.3	0.9988	0.043	-50.0
3',4'-CH_3	96.4	97.8	99.3	100.8	102.3	49.1±0.3	-148.6±1.0	0.9994	0.033	-47.3
4'-OCH_3	96.4	98.0	99.5	101.0	102.5	48.1±0.4	-152.0±1.5	0.9986	0.049	-48.3
4-Cl	93.1	94.7	96.4	98.0	99.6	41.8±0.5	-161.4±1.6	0.9977	0.055	-51.3
2'-CH_3	99.6	98.2	99.8	101.5	103.1	45.6±0.1	-160.5±1.7	0.9986	0.015	-51.0
2'-OCH_3	97.1	98.7	100.3	101.8	103.4	47.7±0.2	-155.5±6.4	0.9956	0.026	-49.4
2'-Cl	94.1	95.7	97.4	99.1	100.7	41.3±0.5	-166.0±1.7	0.9965	0.058	-52.8

Table 5

Determining of Isokinetic Temperature. Correlation Parameters of y = a+bx Equations of Dependence of Kinetic and Activation Parameters of Alkaline Hydrolysis of Methyl Ester Derivatives of 4-Nitro-N-Phenylanthranilic Acid and Isokinetic Temperature β.

x	y	a	b	r	S	β,K
$\log k_{318}$	$\Delta H^{\neq}$	$(12.8\pm1.2)\cdot10^3$	$(-11.8\pm0.6)\cdot10^3$	0.935	1.04	655
$\log k_{328}$	$\Delta H^{\neq}$	$(14.7\pm1.9)\cdot10^3$	$(-12.3\pm0.8)\cdot10^3$	0.914	1.18	672
$\log k_{338}$	$\Delta H^{\neq}$	$(18.6\pm2.3)\cdot10^3$	$(-11.8\pm0.9)\cdot10^3$	0.856	1.51	745
$\log k_{348}$	$\Delta H^{\neq}$	$(16.6\pm2.0)\cdot10^3$	$(-14.0\pm0.9)\cdot10^3$	0.898	1.29	664
$\log k_{358}$	$\Delta H^{\neq}$	$(18.8\pm1.9)\cdot10^3$	$(-14.3\pm1.0)\cdot10^3$	0.892	1.32	690
$\Delta S^{\neq}$	$\Delta H^{\neq}$	$(125\pm4)\cdot10^3$	515 ± 22	0.952	0.89	515
1/T	ρ	-1.03 ± 0.046	680 ± 15	0.990	0.015	660

beginning of thermodynamics ($\Delta G^{\neq}$) are given in Table 4. The high negative values of $\Delta S^{\neq}$ confirm the $B_{AC}2$ mechanism of hydrolysis with the formation of a highly regulated transition state. A comparatively small $\Delta H^{\neq}$ value refers to the synchronism of the reaction studied. The effect of the substituent's nature on the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is similar to those on E_A and ln A. The free activation energy ($\Delta G^{\neq}$) will decrease if the electron acceptor substituents are introduced. It is worth mentioning that the entropy and enthalpy contributions into the $\Delta G^{\neq}$ value are almost equal.

In order to check the existence of the isokinetic correlation for the 3'- and 4'- substituents of the reaction series studied (the number of the 2'- substituents is too small to obtain statistically reliable data), the existence of the linear correlation between the $\Delta H^{\neq}$ - log k_T, $\Delta H^{\neq}$ - $\Delta S^{\neq}$, and $\rho - \frac{1}{T}$ (Table 5) was studied. The data of these tables confirm the isokinetic correlation. The isokinetic temperature $\beta = 640 \pm 42$K is higher than the studied temperature range, thus evidencing about the enthalpic control of the alkaline hydrolysis reaction of methyl esters of 4-nitro-N-phenylanthranilic acid.

Table 6.

Determining of Isokinetic Temperature β. Correlation Parameters of Equation log k_{T_2} = const + x·log k_{T_1} of Alkaline Hydrolysis Reaction of Methyl Ester Derivatives of 4-nitro-N-phenylanthranilic Acid

Temperature, K		x	r	S	β,K
T_1	T_2				
318	328	0.935	0.9922	0.027	596
318	348	0.804	0.9923	0.023	569
318	358	0.786	0.9935	0.021	666
328	348	0.857	0.9961	0.016	549
328	358	0.835	0.9939	0.020	667
338	358	0.861	0.9943	0.019	566

Experimental

Reagents: The purity and purification level control of the solvents have been described earlier[1]. Methyl esters of 4-nitro-N-phenylanthranilic acid were synthesized according to the known methods[5]. Their purity was checked by means of thin layer chromatography (systems dioxane-hexane 1:1 chlorophorm- acetone 1:1) on the "Silufol" plates using the elemental analysis.

Kinetic measurements were conducted according to methods[1]. The concentration of sodium hydroxide was determined by means of potentiometric titration with the aqueous solution of HCl and using the glass ESL-43-074 and chlorosilver EVL-1ML electrodes on an ionometer EV-74. The kinetics of alkaline hydrolysis reaction was studied at 45,55,65,75, and 85°C. The experiments were repeated three times, including 6-8 measurements each (depth of transformation was not less than 80%). The accuracy of the obtained parameters was estimated by means of statistics of small sets (with a 0.95 probability). Linear equations were treated applying the least squares method on a micro computer "MK-52" using standard programs[6].

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Organic Reactivity
Vol. 24 2(86) 1987

REACTIVITY OF AROMATIC AND HETEROCYCLIC DERIVATIVES OF HYDRAZINE
VI. KINETICS OF BENZOYLATION REACTIONS OF HYDRAZIDES OF 4-NITRO-N-(R-PHENYL)-ANTHRANILIC ACIDS

A.N. Gaidukevich, E.N. Svechnikova, and G. Sim
Kharkov State Pharmaceutical Institute, Kharkov, the Ukrainian S.S.R.

Received August 19,1987

The kinetics of benzoylation reaction of 4-nitro-N-(R-phenyl)-anthranilic acids' hydrazides in chlorophorm has been studied in the temperature range of 298-328 K. The reaction obeys the second order kinetic equation for irreversible reactions, thus enabling to calculate the bimolecular rate constants in case of the all temperatures studied. The energies of enthalpy, entropy and the free activation energy were found. The effects of the substituents' state and nature in hydrazide molecule on the kinetic parameters of acylation reaction have also been studied. The Hammett equation proved to hold in case of this reaction series. We also established the existence of the isokinetic relationship with the enthalpic control type.

In order to continue our research[1-5] into the reactivity of aromatic and heterocyclic derivatives of hydrazine, characterized by different types of biological activity[6,7], the kinetics of benzoylation reaction of 4-nitro-N-(R-phenyl)--anthranilic acids' hydrazides (Table 1) has been studied in

chlorophorm in the temperature range of 298-328 K.

The reaction proceeds as follows:

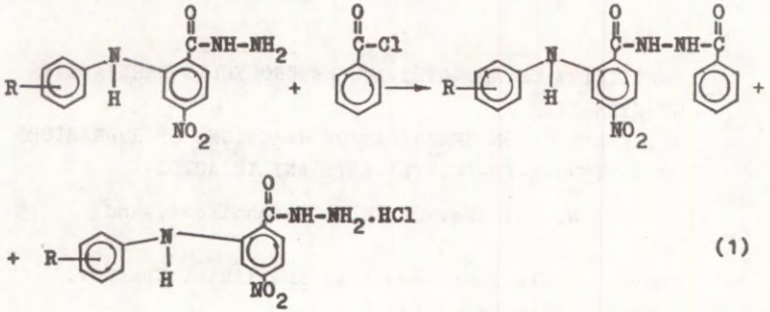

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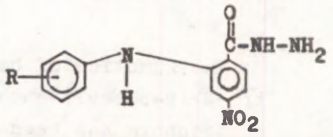
Table 1

Hydrazides of 4-Nitro-N-(R-phenyl)-Anthranilic Acids



R	Melting point °C	% N found	Brutto formula	% N calculated	Rf_1	Rf_2
H	162-4	20.5	$C_{13}H_{12}N_4O_3$	20.6	0.45	0.53
4'-CH_3	153-5	19.5	$C_{14}H_{14}N_4O_3$	19.6	0.44	0.52
4'-OCH_3	169-71	18.5	$C_{14}H_{14}N_4O_4$	18.5	0.41	0.42
4'-Cl	157-9	18.2	$C_{13}H_{11}ClN_4O_3$	18.3	0.41	0.51
3',5'-CH_3	133-5	18.6	$C_{16}H_{16}N_4O_3$	18.7	0.47	0.61
3',4'-CH_3	120-2	18.6	$C_{16}H_{16}N_4O_3$	18.7	0.48	0.64
2'-CH_3	171-3	19.5	$C_{14}H_{14}N_4O_3$	19.6	0.47	0.34
2'-OCH_3	170-2	18.5	$C_{14}H_{14}N_4O_4$	18.5	0.45	0.22
2'-Cl	104-6	18.2	$C_{13}H_{11}ClN_4O_3$	18.3	0.49	0.33

Rf_1 - in the system ethyl acetate-chlorophorm 40:10

Rf_2 - in the system hexane-isopropanol 80:30

The reaction rate constants were calculated according to the variation of hydrazide concentration in time, determined by means of nitritometric potentiometric titration. The technique of kinetic measurements has been described earlier. The kinetics of benzoylation of 4-nitro-N-(R-phenyl)-anthranilic acid hydrazides obeys the second order reaction for irreversible reactions. It can be proved by the following facts:

a) stability of reaction rate constant values (Table 2) at different time moments, calculated according to equation

$$k = \frac{1}{2\beta t} \cdot \left(\frac{1}{a-x} - \frac{1}{a} \right), \qquad (2)$$

where a is the initial concentration of benzoyl chloride in mol/l;

x denotes the concentration of benzoyl chloride at a certain time moment (s; mol/l);

β is a correction to the thermal expansion of chlorophorm;

b) linear dependence between the inverse current concentration of the reagent in time (see Fig. 1);

c) the reaction order can be determined as follows[8]:

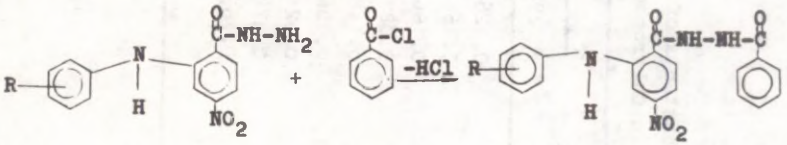
$$n = 1 + \frac{\log \tau_1 - \log \tau_2}{\log a_2 - \log a_1} \qquad (3)$$

n is the reaction order;

τ_i denotes the time of the 50% proceeding of the reaction in case of the initial concentration of benzoyl chloride a_i mol/l.

The obtained date show that the reaction studied turned out to be kinetically complicated and proceeds in two stages:

stage I



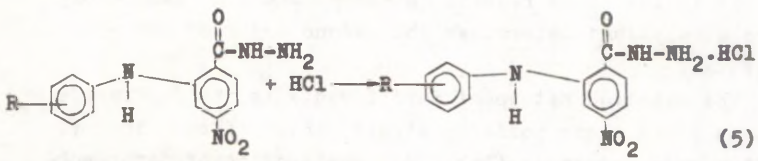
(4)

Table 2

Rate Constants of Benzoylation Reaction of Hydrazides of 4-nitro-N-(R-phenyl)-Anthranilic Acids in Chlorophorm at Various Temperatures

R	k, $l \cdot mol^{-1} \cdot s^{-1}$ at T, K			
	298 K	308 K	318 K	328 K
H	0.126±0.010	0.200±0.017	0.299±0.016	0.415±0.024
4'-CH_3	0.166±0.021	0.245±0.028	0.356±0.011	0.502±0.019
4'-OCH_3	0.186±0.011	0.288±0.019	0.417±0.021	0.582±0.016
4'-Cl	0.087±0.011	0.145±0.012	0.224±0.016	0.322±0.017
3',5'-CH_3	0.148±0.017	0.232±0.019	0.349±0.014	0.462±0.029
3',4'-CH_3	0.186±0.023	0.279±0.014	0.380±0.019	0.543±0.019
2'-CH_3	0.324±0.019	0.380±0.016	0.468±0.021	0.575±0.022
2'-OCH_3	0.372±0.016	0.460±0.022	0.562±0.017	0.627±0.024
2'-Cl	0.166±0.011	0.218±0.012	0.286±0.015	0.353±0.028

stage II



(5)

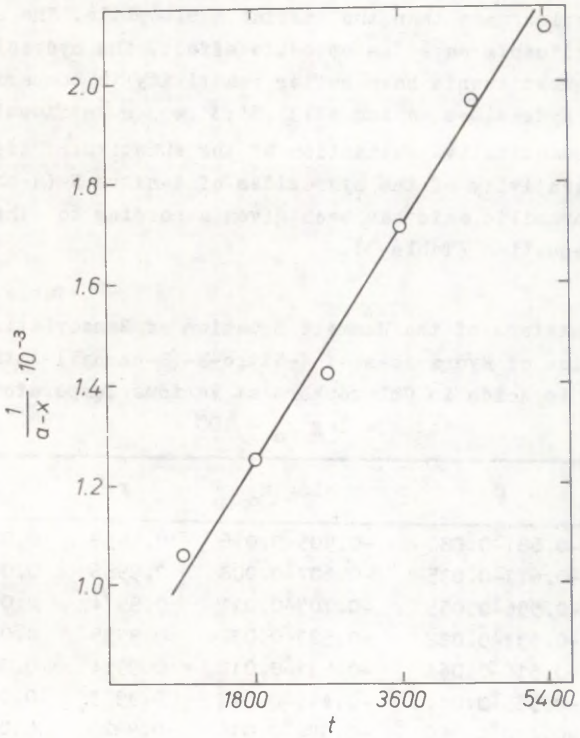


Fig. 1. Dependence of the inverse value of the current concentration $(\frac{1}{a-x})$ on time (t) in case of acylation of the 4-nitro-N-(R-phenyl)-anthranilic acid hydrazide with b = $2.5 \cdot 10^{-3}$ mol/l benzoyl chloride of a = = $1.25 \cdot 10^{-3}$ mol/l in chloroform at 298 K.

It is the first reaction stage proceeding remarkably more slowly that determines the second order of the process in total.

The electron nature of substituents in the hydrazide molecule and their position significantly affect the reaction rate constants (Table 2). Application of donor substituents accelerates the rate of the process, i.e. donor substituents in the nucleophile molecule stabilize the activated complex more than the initial nucleophile. The acceptor substituents have the opposite effect. The hydrazines with 2'-substituents have better reactivity in comparison with the hydrazines having 4';3',5';3',4' substituents.

The quantitative estimation of the substituent effect on the reactivity of the hydrazides of 4-nitro-N-(R-phenyl)-anthranilic acid has been given according to the Hammett equation (Table 3).

Table 3

Parameters of the Hammett Equation of Benzoylation Reaction of Hydrazides of 4-Nitro-N-(R-phenyl)-Anthranilic Acids in Chlorophorm at Various Temperatures

$$\log k = \log k_o + \Delta\rho\sigma$$

T,K	ρ	$\log k_o$	r	S
298[a]	-0.681±0.080	-0.905±0.016	0.9959	0.0128
298[b]	-0.671±0.035	-0.607±0.008	0.9986	0.0041
308[a]	-0.596±0.055	-0.705±0.011	0.9974	0.0088
308[b]	-0.631±0.082	-0.523±0.032	0.9935	0.0267
318[a]	-0.516±0.064	-0.531±0.012	0.9954	0.0102
318[b]	-0.565±0.044	-0.419±0.042	0.9909	0.0285
328[a]	-0.498±0.080	-0.384±0.016	0.9923	0.0128
328[b]	-0.512±0.081	-0.334±0.018	0.9988	0.0095

a - data for 3',4',5' derivatives were correlated

b - data for 2' derivatives were correlated

The values of reaction parameter ρ are negative, thus confirming the nucleophilic substitution mechanism of S_N2 of the reaction studied. We did not succeed in conducting a general correlation for the compounds with 3',4'- and 2'- substituents in the hydrazine molecule (Fig. 2), but separate correlation of substituents with the 3',4'- and 2'-substituents gives a good statistical reliability. It should be mentioned that the ρ values for the compounds with 3',4'- substituents and 2'-substituents in a nucleophile molecule are quite close.

Insignificant values of reaction parameter ρ evidence about a small susceptibility of the reaction series to the effect of the substituent's nature in the nucleophile molecule. It is worth mentioning that the absolute values of ρ are dropping when the temperature increases.

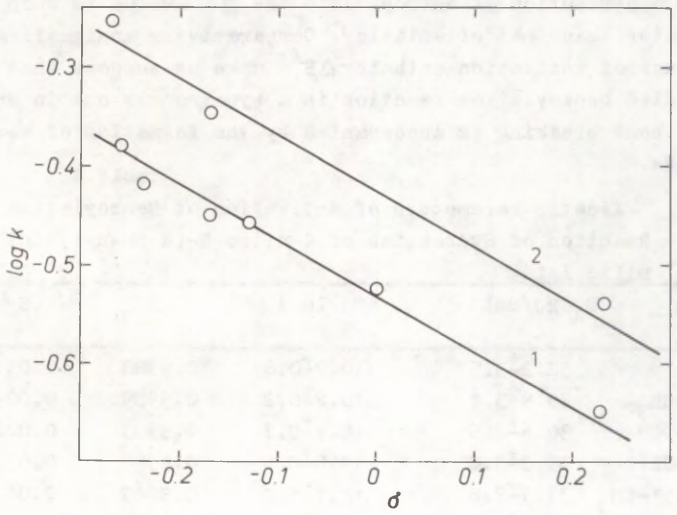


Fig. 2. Dependence of log k-f(σ) at 318 K for 3',4',5'-(1) and 2'-(2) substituents in the molecule of 4-nitro-N-(R-phenyl)-anthranilic acid hydrazide.

The polyterms of rate constant logarithms are linear, so it was possible to find the activation energy - E_A. and the preexponential factor A according to the Arrhenius equation (Table 4). If the electron-donor substituents are conducted into the nucleophile molecule, the E_A value will decrease. In the case of 2'-substituents it is expressed more sharply but the linear correlation between the E_A and σ Hammett constants is statistically doubtful.

The Eyring[9] equation has been applied in order to calculate the activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$). The free energy of activation was calculated according to the second beginning of thermodynamics. The obtained data are given in Table 5. The values of free activation energy $\Delta G^{\neq}$ are quite close for nucleophiles having substituents with different nature and position in a molecule in case of all the temperatures studied. It is interesting to mention that the contribution of entropy into the $\Delta G^{\neq}$ value is much greater than that of enthalpy. Comparatively insignificant values of activation enthalpy $\Delta H^{\neq}$ make us suppose that the studied benzoylation reaction is a synchronous one in which the bond breaking is accompanied by the formation of new bonds.

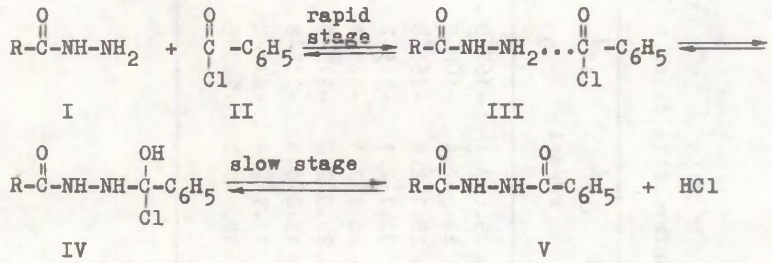
Table 4

Kinetic Parameters of Activation of Benzoylation Reaction of Hydrazides of 4-nitro-N-(R-phenyl)-Anthranilic Acids

R	E_A kJ/mol	ln A	r	S
H	32.2 ± 3.5	10.9 ± 0.8	0.9988	0.031
4'-CH_3	29.9 ± 3.4	10.2 ± 0.2	0.9989	0.004
4'-OCH_3	30.6 ± 2.5	10.7 ± 0.7	0.9993	0.022
4'-Cl	35.3 ± 3.8	11.8 ± 0.9	0.9988	0.033
3',5'-CH_3	31.1 ± 2.8	10.7 ± 1.2	0.9949	0.061
3',4'-CH_3	28.5 ± 2.7	9.82 ± 0.21	0.9991	0.024
2'-CH_3	15.6 ± 1.9	5.15 ± 0.19	0.9965	0.026
2'-OCH_3	14.3 ± 1.3	4.31 ± 0.14	0.9938	0.031
2'-Cl	20.5 ± 1.6	6.49 ± 0.24	0.9993	0.015

The effect of the substituents' nature and their position in the hydrazide molecule on the $\Delta H^{\neq}$ value is analogous to the same effect on the E_A which has been already previously discussed. High negative $\Delta S^{\neq}$ values is another evidence to prove the existence of the S_N2 mechanism of nucleophilic substitution with the formation of a highly regulated state.

To sum up the aforesaid as well as the literature data[8], the following mechanism of benzoylation reaction of hydrazides of 4-nitro-N-(R-phenyl)-anthranilic acids can be suggested:



The reaction starts with the nucleophilic attack of hydrazide (I) at the acylating agent (II). The associative process (rapid stage) results in the formation of the molecular compound (III) which is transformed into the enol form (IV) and then follows a slow breakage of the leaving group (HCl) and the reaction yield is formed.

In the reaction series investigated, holds the isokinetic correlation. It is confirmed by the existence of the linear correlation between the $\Delta H^{\neq}$ - log k_T, $\Delta H^{\neq}$ - $\Delta S^{\neq}$, E_A-log A, ρ - 1/T, log k_{T_2} -log k_{T_1} (Table 6) and proved by the method of regression analysis[1] for the compounds with 3',4',5'-substituents in a molecule (the number of compounds with 2'-substituents is not great enough to get statistically valuable data). The isokinetic temperature $\beta = 453 \pm 16$ is higher than the experimental range, thus making it possible to presume the possibility of enthalpy control in case of the studied benzoylation reaction of hydrazides of 4-nitro-N-(R-phenyl)-anthranilic acids.

Table 5

Thermodynamic Parameters of Activation $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$ of Benzoylation Reaction of Hydrazides of 4-Nitro-N-(R-phenyl)-Anthranilic Acids

R	$\Delta G^{\neq}$ kJ/mol				$\Delta H^{\neq}$ kJ/mol	$\Delta S^{\neq}$ J/0	r	S	$T, \Delta S^{\neq}$ kJ/mol
	298K	308K	318K	328K					298K
H	77.9	79.5	81.1	82.3	29.6±3.4	-162±8	0.9986	0.030	-48.3
4'-CH_3	77.4	79.0	80.7	82.4	27.3±2.4	-168±2	0.9987	0.044	-50.1
4'-OCH_3	77.0	78.6	80.3	81.9	28.1±2.4	-164±8	0.9992	0.021	-48.9
4'-Cl	78.9	80.4	82.0	83.5	32.7±2.1	-155±2	0.9986	0.035	-46.2
3',5'-CH_3	77.6	79.2	80.9	82.5	28.4±2.1	-165±16	0.9965	0.0145	-49.2
3',4'-CH_3	77.2	78.9	80.6	82.3	25.9±2.8	-172±2	0.9987	0.025	-51.3
2'-CH_3	75.9	78.0	80.1	82.2	13.0±0.3	-211±8	0.9950	0.028	-62.9
2'-OCH_3	75.5	77.6	79.8	81.9	11.7±0.4	-214±8	0.9900	0.033	-63.8
2'-Cl	77.5	79.5	81.5	83.5	17.9±0.2	-200±6	0.9988	0.016	-59.6

Table 6

Determining of Isokinetic Temperature (β). Correlation Parameters of Equations y=a+bx of Benzoylation Reaction of Hydrazides of 4-Nitro-N-(R-phenyl)-Anthranilic Acids.

x	y	a	b	r	S	β,K
$\Delta S^{\neq}$	$\Delta H^{\neq}$	$(111 \pm 10)\cdot 10^3$	497 ± 40	0.9271	178	497
ln A	E	-5.12 ± 0.70	3.41 ± 0.34	0.9857	0.439	430
$\log k_{298}$	$\Delta H^{\neq}$	$(14.0 \pm 0.6)\cdot 10^3$	$(-17.5 \pm 3.5)\cdot 10^3$	0.9487	822	443
$\log k_{308}$	$\Delta H^{\neq}$	$(16.0 \pm 0.7)\cdot 10^3$	$(-19.6 \pm 1.0)\cdot 10^3$	0.9292	961	441
$\log k_{318}$	$\Delta H^{\neq}$	$(18.2 \pm 0.7)\cdot 10^3$	$(-21.7 \pm 1.4)\cdot 10^3$	0.8953	759	442
$\log k_{328}$	$\Delta H^{\neq}$	$(21.1 \pm 0.5)\cdot 10^3$	$(-22.7 \pm 1.4)\cdot 10^3$	0.9049	721	454
$\log k_{298}$	$\log k_{328}$	0.276 ± 0.036	0.729 ± 0.011	0.9927	0.0125	450
$\log k_{308}$	$\log k_{338}$	0.206 ± 0.024	0.837 ± 0.021	0.9960	0.0093	491
I/T^a	ρ	1.41 ± 0.10	-618 ± 28	0.9752	0.0227	440
I/T^b	ρ	1.50 ± 0.17	-658 ± 11	0.9975	0.0076	438

a - for 3',4',5' - substituents

b - for 2' substituents

Experimental

Reagents. Purification, drying and testing of purity level of chlorophorm and benzoyl chloride have been described earlier[1].

Hydrazides were synthesized according to the known techniques[10,11]. Their purity was tested chromatographically, by means of elemental analysis, and determining the melting points (Table 1).

Kinetic measurements were conducted according to methods[1]. The concentration of hydrazides was determined by means of potentiometric titration with a 0.01 M solution of sodium nitrate EVL-1M1 with platinum ETPL-01 M and chlorosilver electrodes on an ionometer EV-74. Reaction kinetics was studied at temperatures 298,308,318,328 K. Each experiment was repeated three times, including 6-8 measurements each, the depth of transformations was up to 80%. The accuracy of the obtained parameters was assessed by means of mathematical statistics for small sets[12] (the reliability level being 0.95) Thermodynamic parameters of activation were calculated according to the known formulae applying the least squares' method. Linear equations were treated by means of the least squares method on a micro computer "Electronika MK-52", applying standard programs[14].

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Organic Reactivity
Vol. 24 2(86) 1987

EFFECT OF PHENOLS ON DECOMPOSITION RATE OF SODIUM 6,8-DINITRO-1,4-DIOXASPIRO[4,5]DECA-6,9-DIENATE

I.V. Shakheldyan, S.S. Gitis, and A.I. Glaz
Tula State Teacher Training Institute

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Decomposition kinetics of sodium 0,8-dinitro-1,4-dioxaspiro[4,5]deca-6,9-dienate has been studied in binary mixtures of dimethylsulfoxide - protonic components - phenols whose nuclei contain various substituents. It has been shown that the decomposition reaction of 2,4-dinitrospirocomplex proceeds according to the bimolecular mechanism and largerly depends on the position of substituents in a phenol nucleus, affecting either the pK_{α} values of phenols or influencing the steric factors of proton transfer.

Recently we have shown[1] that the decomposition of dinitrospiro complexes in the presence of protonic complexes (alcohols and water) is analogous to the Jackson-Meisenheimer complexes, when one of the Ar-O[2] bonds is broken. The reaction rate is affected both by the pK_{α} of a proton-donor component depending on the nature of the hydrocarbon radical of alcohol, and by the effects connected with their space structure.

In order to find the effects of the other agents which have greater acidity than alcohols, we have studied the dependence of the disclosure rate of spirocycle on the nature and concentration of the phenols whose nuclei contain dif-

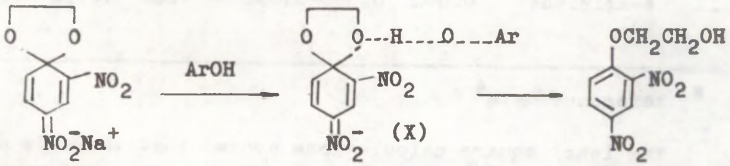
ferent substituents.

The measurements were carried out spectrophotometrically in the visible range where the sodium 6,8-dinitro-1,4-dioxaspiro[4,5]deca-6,9-dienate complex absorbs while the glycolic ether forming during the disclosure of the cycle will not absorb. Weakening of the absorption bond intensity in time refers to the first order of the reaction complex being decomposed. Rate constants were measured at $\pm$5% accuracy.

The linear dependence of the pseudofirst order rate constant on the phenol concentration indicates, that the reaction has the first order concerning also its protonic component.

The Brønsted graph of the $\log k_{NA}$ dependence on the pK_α value is given in Fig. 1. The Brønsted coefficient α equals 0.52 according to the slope of the straight line in the given coordinates.

Thus, our studies show that the reaction is a bimolecular one, in the case of which the proton transfer with formation of X (scheme 1) appears to be the limiting step, followed by a rapid breaking of the C-O bond.



Scheme 1

The results of kinetic measurements presented in Table 1 evidence about a direct dependence of the decomposition rate of the observed spiro complex on the acidity and structure of the phenols used. The reactivity of the latter varies from 1-9 (Table 1).

The rest of the pK_α values were obtained experimentally from the dependence of the log k value of the decomposition rate on the pK_α using graphic methods. This dependence was got when applying phenols I-IV and VIII with the known pK_α values (Fig. 1).

Table 1

Kinetic Parameters of 2,4-Dinitrospiro Complex Decomposition Reaction Caused by the Phenols of Various Structure

No	Phenols	S mole/l	$k \cdot 10^2, s^{-1}$	K l/mole·1	pK_α	σ^3
I	4-bromophenol	0.001	1.298 ± 0.067	12.98	9.36*	0.30
II	4-chloro-phenol	0.001	1.164 ± 0.252	11.64	9.38*	0.28
III	phenol	0.002	1.070 ± 0.019	5.35	10.0*	0
IV	2-methylphe-nol	0.002	0.690 ± 0.051	3.45	10.29*	-0.17
V	3,4-dimethyl phenol	0.002	0.695 ± 0.026	3.48	10.37	-0.209
VI	4-ethyl phe-nol	0.002	0.693 ± 0.051	3.42	10.39	-0.151
VII	3,5-dimethyl phenol	0.002	0.464 ± 0.024	2.32	10.68	-0.138
VIII	2,4,6-tri-methyl phe-nol	0.002	0.169 ± 0.018	0.845	10.8*	-0.44
IX	4-aminophe-nol	0.002	0.360 ± 0.032	1.80	10.92	-0.38

* Reference data[4]

The least square calculations proved that there is a satisfactory correlation dependence between the log k and pK_α of the phenols given in Table 1(r=0.952; S=0.173). 2,4,6-trimethylphenol does not evidently suit this dependence (Fig. 1). A lower reactivity of the latter and 2-methylphenol are most probably caused by the screening effect of ortho-methyl groups[5] which complicate the hydrogen bond formation between the oxygen atoms of spirocycle and the OH group of molecules of these phenols. It should be pointed out that if 2,4,6-trimethylphenol is not taken into consideration, a remarkable improvement of the correlation dependence (r=0.987; S=0.058) can be observed.

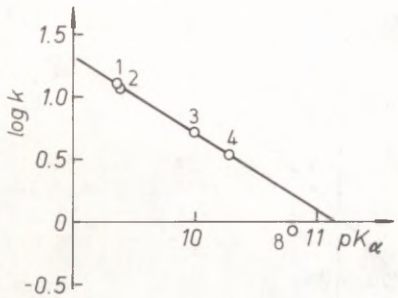


Fig. 1. Dependence of log k on the pK$_\alpha$ of phenols for dinitrospiro complex decomposition. Marking of points corresponding to that of Table 1.

Comparison of the data given in Table 1 (log k) with the σ^o values (Fig. 2) shows that in all series studied, the effect of substituted phenols obey the Hammett-Taft equation (r=0.964; S=0.107).

According to Fig. 2, the compounds with the substituents in 2-position (IV and VIII) tend to deviate from the common correlation dependence. It can be explained[5] by the ambiguity of the σ^o values for the ortho-substituted phenyls caused by the effect of steric factors on the reactivity of the compounds in the process.

Exclusion of the phenols, containing substituents in the 3rd position (V and VII) brings about a remarkable increase of the correlation coefficient r=0.983; s=0.0874, (if the methyl radical is in meta position, the contribution of the conjugation effect drops in comparison with the ortho-substituents.).

A considerably high value of the reaction constant ρ (ρ=1.404) refers to a remarkable polarity of the transition

state of the process.

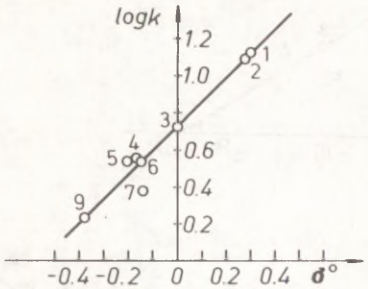


Fig. 2. Dependence of log k on the σ^{o} value of substituents in case of decomposition reaction of spirocyclic complex at 25°C. Marking of points corresponds to those of Table 1.

Thus, the rate of cycle breaking depends largerly on the position of the substituents in a phenol nucleus affecting either the pK_{α} value of a phenol, or the steric factors of proton transfer.

Experimental

Sodium 6,8-dinitro-1,4-dioxaspiro[4,5]deca-6,9-dienate was obtained by means of intramolecular cyclization, under the effect of sodium tert.-butylate on the dioxan solution of 1-(β-oxyethoxy)-2,4-dinitrobenzene. 1-(β-oxyethoxy)-2,4-dinitrobenzene was obtained according to the known methods[6].

Dimethylsulphoxide was purified as described in[7].

Reactive phenols, whose purity level was assessed by the methods of thin layer chromatography and via determining the melting points corresponding to the literature data were used.

Kinetic measurements were conducted under pseudomonomolecular conditions at a substantial residue of the protonic component. Rate constants were calculated according to

the first order equation[8]. The rate constants presented in Table 1 are the mean values of three parallel measurements. The accuracy of kinetic measurements was tested using the methods of mathematical statistics, the reliability coefficient being 0.95. The variability coefficient of calculating the reaction rate constants did not exceed 5-7%.

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Organic Reactivity
Vol. 24 2(86) 1987

NUCLEOPHILIC SUBSTITUTION AT TETRACOORDINATED ATOM OF PHOSPHORUS. KINETICS AND MECHANISM OF REACTIONS OF OH- AND NH-NUCLEOPHILES WITH DIPHENYLCHLOROPHOSPHATE CATALYZED BY PYRIDINE N-OXIDE IN ACETONITRILE

T.N. Solomoichenko, V.A. Savyolova, T.V. Ved, and Yu.S. Sadovskij

Institute of Physical Organic Chemistry and Coal Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk

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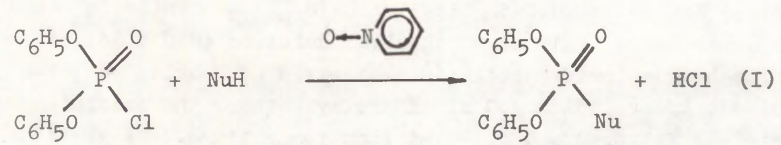
Kinetics of hydrolysis, methanolysis and aminolysis of diphenylchlorophosphate, catalyzed by pyridine N-oxide in acetone at 25°C has been studied spectrophotometrically and conductometrically. Inhibiting effect of a similar chloride ion and the change of rate limiting stage from the intermediate product formation up to the nucleophilic attack proportionally to the decrease of concentration of the latter were detected. Existence of nucleophilic mechanism of catalysis including the formation of the ionic intermediate, diphenyl pyridinium phosphate chloride, can be suggested on the basis of these results.

It is known that in the aprotic solvents, pyridine N-oxides function as highly effective catalysts of the amino-

lysis of functional derivatives of carbonic (ArCOX, X=Cl,Br)[1] and sulphonic ($ArSO_2X$, X=Cl, Br, OSO_2Ar)[2,3] acids. It has been proved that in the case of these processes holds the nucleophilic mechanism of catalysis, the rate determining stage being the amine interaction with either acilic or sulphonylic intermediates which form quite rapidly during the first pre-equilibrium stage from the substrate and the pyridine N-oxide. There are no kinetic data in the literature on the similar kind of processes of nucleophilic substitution at the tetracoordinated phosphorus atom in the aprotic solvents.

We studied the kinetic regularities and the mechanism of the diphenylchlorophosphate (DPCP) reactions with OH-(water, methanol), and NH-(3-nitroaniline, diethylamine) nucleophiles (NuH), catalyzed by pyridine N-oxide in acetonitrile at 25°C:



NuH = H_2O, CH_3OH, $(C_2H_5)_2NH$, $3\text{-}NO_2C_6H_4NH_2$.

During the catalytic processes of hydrolysis and methanolysis, the precipitating hydrogen chloride combines with pyridine N-oxide. In the catalytic aminolysis reactions forms amine hydrochloride (pyridine N-oxide does not undergo any transformations in the course of the process). Thus, in the case of the DPCP reaction with diethylamine catalyzed by pyridine N-oxide, we observed stable optical density of the latter in the course of the reaction (the wave length being 275 nm).

We have shown[4] that in the dichloromethane and acetonitrile, pyridine N-oxides efficiently accelerate both the aminolysis and hydrolysis of the DPCP. It has been mentioned that in the used solvents, dehydrated according to the ordinary methods, the DPCP hydrolysis, catalyzed by pyridine N-oxides, proceeds at a remarkably high rate because of the residual moisture. This fact should be taken into consideration when studying the catalytic interaction of DPCP with other

nucleophiles in aprotic media.

Experimental

DPCP[5] and pyridine N-oxide[6] were synthesized and purified according to the known methods. 3-nitroaniline of a "chemically pure" grade was recrystallized from ethanol; diethylamine was kept over the metallic sodium and distilled over its fresh portion. Acetonitrile was purified according to methods[7], its residual water content being approximately $5 \cdot 10^{-3}$ mol·l^{-1} (according to the method of Fischer).

The products of hydrolysis and methanolysis of the DPCP were found and identified.

Hydrolysis of DPCP. 15 ml of the pyridine N-oxide (0.015 moles) and water (0.015 moles) solution in acetonitrile at 25°C was added to 15 ml of the DPCP solution (0.015 moles). White hydrochloride precipitate of pyridine N-oxide was obtained. After adding 150 ml of diethyl ether, the precipitate was filtered and dried at room temperature. The yield was 1.9 g (96.4 %), its melting point being 180-182°; (in ref.[8] 178-180°). % found: C 45.69; H 4.90; Cl 26.64; N 10.57. C_5H_6ClNO. % calculated: C 45.65; H 4.59; Cl 26.95; N 10.65. After evaporation of the filtrate, was obtained 3.5 g (93.3%) of diphenylphosphoric acid; melting point 64° (in ref.[9] 63°). % found: C 57.85; H 4.45; P 12.54. $C_{12}H_{11}O_4P$. % calculated: C 57.61; H 4.43; P 12.38.

Methanolysis of DPCP. 10 ml of the pyridine N-oxide (0.0075 moles) and methanol (0.0075 moles) solution was added to 10 ml of the DPCP solution (0.0075 moles) in acetonitrile at 25°C. The reaction products were separated the same way as in case of hydrolysis. 0.96 g (98 %) of pyridine N-chloride of hydrochloride and 1.87 g (94.4 %) of methyldiphenylphosphate were obtained, the boiling point was 146-150° (1mm), (in ref.[10] 151±5° (1mm)). % found: C 59.02; H 5.01; P 11.86; $C_{13}H_{13}O_4P$. % calculated: C 59.10; H 4.96; p 11.72.

Separation of the DPCP aminolysis products in presence of pyridine N-oxide has been described earlier[4].

Kinetic experiments were carried out in two concentration ranges: 1) the concentrations of DPCP and nucleophilic reagent (water, methanol) remarkably exceeded the concentration of pyridine N-oxide; 2) the concentrations of pyridine N-oxide and nucleophilic reagent (water, amine) remarkably exceeded the DPCP concetration. Because of that, two methods of kinetic measuring were applied.

In the first case, the process rate was monitored spectrophotometrically according to the pyridine N-oxide decrease which reacts with hydrogen chloride formed. Optical density was measured on a spectrophotometer SF-26 in the range of 275 nm. The Lambert-Bouguer-Beer law holds both in case of acetonitrile ($\varepsilon = 12{,}600 \pm 500$ $l \cdot mole^{-1} \cdot cm^{-1}$, $s_o = 4 \cdot 10^{-2}$, $r = 0.995$, $N = 8$) and the acetonitrile containing water additions up to 1.5 $mole \cdot l^{-1}$ (e.g., if $[H_2O] = 0.4$ $mole \cdot l^{-1}$, $\varepsilon = 13{,}040 \pm 160$, $s_o = 2.1 \cdot 10^{-2}$, $r = 0.999$, $N = 14$). In the acetonitrile without water additions, the hydrolysis was in a number of cases monitored according to the accumulation of the reaction product - the hydrolchloride of pyridine N-oxide ($\lambda = 235$ nm, $\varepsilon = 4340 \pm 180$ $l \cdot mole^{-1} \cdot cm^{-1}$, $s_o = 3.3 \cdot 10^{-2}$, $r = 0.997$, $N = 6$).

The pseudofirst order rate constants $k^I(s^{-1})$ were calculated as follows:

$$k^I = \frac{1}{t} \ln \frac{D_o - D_\infty}{D_t - D_\infty} , \qquad (2)$$

where D_∞, D_o, D_t denote the optical density of the solution at the completion of the reaction, at the initial time moment t, respectively.

In the second case, the reaction was controlled conductometrically according to the accumulation of hydrogen chloride (in the form of amine hydrochloride salt or pyridine N-oxide). The resistance of the solution was measured applying the apparatus described in[11]. The k^I constants were calculated according to the formula:

$$k^I = \frac{1}{t} \ln \frac{\frac{1}{R_\infty} - \frac{1}{R_o}}{\frac{1}{R_\infty} - \frac{1}{R_t}}, \qquad (3)$$

where R_∞, R_o and R_t denote the resistance of the solution at the completion of the reaction and at the initial time moment t, respectively.

The kinetics of the noncatalytic processes of the hydrolysis, methanolysis and diethylaminolysis of DPCP was studied conductometrically if [DPCP] $\ll$ [NuH], the interaction kinetics of DPCP with 3-nitroanile was investigated spectrophotometrically according to the decrease of the optical density of arylamine (λ = 375 nm, ε = 1800±35, s_o = $2.56 \cdot 10^{-2}$, r = 0.999, N = 8) if [DPCP] $\gg$ [NuH].

Noncatalytic Processes

The rate of the noncatalytic interaction of DPCP with 3-nitroaniline and diethylamine can be described by the second order equation. It is confirmed by the linear dependence in the "k^I - [NuH]" and "k^I - [DPCP]" coordinates, on the basis of which and applying the data of Table 1 have been calculated the bimolecular rate constants k_o^{II} given in the same table.

Table 1

Noncatalytic Interaction of DPCP with Amines in Acetonitrile at 25°C

Nucleophile NuH	[NuH], mole·l^{-1}	[DPCP], mole·l^{-1}	k_o^I, s^{-1}	k_o^{II}, l·mole^{-1}·s^{-1}
3-nitro-	$\approx 5 \cdot 10^{-4}$	0.03	$(0.25 \pm 0.01) \cdot 10^{-5}$	
aniline		0.05	$(0.40 \pm 0.07) \cdot 10^{-5}$	
		0.10	$(0.77 \pm 0.02) \cdot 10^{-5}$	
		0.20	$(1.24 \pm 0.04) \cdot 10^{-5}$	
		0.30	$(2.37 \pm 0.15) \cdot 10^{-5}$	

Nucleophile NuH	[NuH] mole·l^{-1}	[DPCP] mole·l^{-1}	k_o^I, s^{-1}	k_o^{II}, l·mole^{-1}·s^{-1}
		0.33	$(2.40\pm0.06)\cdot10^{-5}$	
		0.66	$(5.22\pm0.05)\cdot10^{-5}$	$(7.83\pm0.28)\cdot10^{-5}$
Diethyl-	1.00	$\approx5\cdot10^{-5}$	1.35 ± 0.02	
amine	1.20		1.64 ± 0.01	
	1.60		2.13 ± 0.21	
	2.20		2.91 ± 0.07	
	2.34		3.12 ± 0.03	
	2.84		3.72 ± 0.06	
	3.34		4.81 ± 0.03	
	4.00		5.10 ± 0.10	13.17 ± 0.63

The rate constants of the noncatalytic reactions of the hydrolysis and methanolysis of DPCP were assessed analogously. In the case of these processes, $k_o^{II} \approx 1\cdot10^{-4} - 1\cdot10^{-5}$ l·mole^{-1}·s^{-1}.

Catalytic Processes

The hydrolysis reaction of DPCP in the presence of pyridine N-oxide (B) in acetonitrile without water additions (the hydrolysis proceeds at the expense of the residual moisture[4]) has a tendency toward a decrease of the observed pseudofirst order rate constants during the process. Such a phenomenon takes place both in conditions [DPCP] $\gg$ [B] (spectrophotometric methods) and [DPCP] $\ll$ [B] (conductometric methods). If $[DPCP]_o = 1.44\cdot10^{-5}$ mole·l^{-1}, the k^I value for the hydrolysis reaction drops 1.5-2 times, the conversion degree being $\approx$ 50 %. Extrapolation of the linear regions of the k^I or $1/k^I$ dependences on x (x is the yield of the product at time moment t) to the zero value of x and also calculation of the corresponding k^I constants from linear dependences $x/t = f(t)$ gives close k^I values at the zero time moment. The k^I values obtained by extrapolation of the constants to the zero x value were used when making the graphs in Figs.1,2.

Comparison of the k^I constants of the processes in the presence of pyridine N- oxide (see Figs. 1-3 and Table 2) and the noncatalytic k_o^I constants shows that in case of the nucleophiles studied (with the exception of diethylamine) the rate of the noncatalytic reaction in the presence of a catalyst can be neglected and the k^I constants can be taken as those characterizing a strictly catalytic process. In the case of diethylamine, in order to characterize the rate of the catalytic process the differences of $k^I - k_o^I$ should be used instead of the k^I values.

The additions of chloride ion, introduced in the form of the lithium chloride salt, dissociating in acetonitrile (K_{ass} = 3500 l·mole^{-1}, 25°C)[12] cause the k^I values to decrease (Fig. 1) but also make them remain stable during the process. The increase of the nucleophilic concentration in the reaction mixture also promotes the k^I stability.

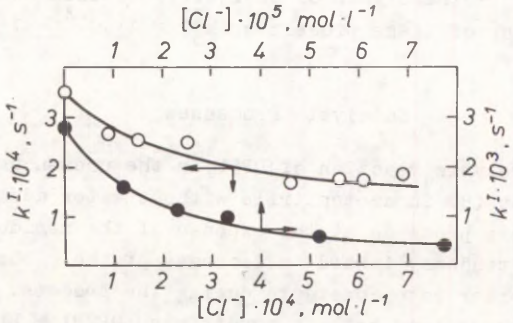
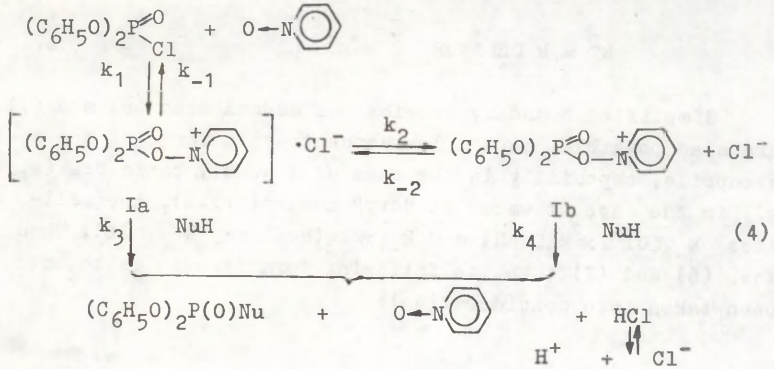


Fig. 1. Dependence of the observed rate constants k^I on the chloride-ion concentration in case of DPCP hydrolysis in acetonitrile, catalyzed by pyridine N- oxide (B) at 25°C.
1 - [DPCP] = $1.17 \cdot 10^{-3}$ mole·l^{-1}, [B] ≈ $6 \cdot 10^{-5}$ mole·l^{-1}
2 - [DPCP] ≈ $5 \cdot 10^{-5}$ mole·l^{-1}, [B] = $8.2 \cdot 10^{-4}$ mole·l^{-1}

It is quite sensible to presume on the basis of the decelerating chloride-ion effect (Fig. 1) that the discussed reaction includes an invertible stage with the chloride-ion formation (which either precedes the rate determining stage or itself determines the rate). The inhibiting action of a similar ion has been discussed in literature as a major criterion of the nucleophilic mechanism of catalysis[13].

The essence of the mechanism applied in the case of the given reaction system is the fact that (c.f.[1-3]) DPCP forms with pyridine N-oxide intermediate product I of ionic nature, i.e. diphenylpyridinephosphate chloride, which (as it can be suggested on the basis of similarity with the N-acetyloxypyridinium salts[14]) exists in acetonitrile in the forms of ion pair Ia and free ions Ib and in the form of the chloride ion (Scheme (4)). In the following stage, the nucleophilic reagent (water, alcohol, amine) attacks intermediates Ia and Ib where the reaction product formation and the regeneration of pyridine N-oxide (in the case of hydrolysis and methanolysis in the form of its hydrochloride salt) take place.

It is noteworthy that the rate of the pyridine N-oxide consumption and the formation of its hydrochloride salt coincide (Fig. 2). It shows that in the course of the process a substantial intermediate I accumulation does not take place (a remarkable scattering of points in Fig. 2 can evidently be explained by the water content not being strictly the same in different portions of "dry" acetonitrile used).



(4)

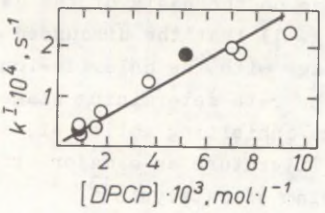


Fig. 2. Dependence of rate constants k^I on DPCP concentration in hydrolysis reaction of DPCP, catalyzed by pyridine N-oxide (B) in acetonitrile containing $\approx 5 \cdot 10^{-3}$ mole$\cdot l^{-1}$ of residual water, 25°C [DPCP] $\gg$ [B]. White points mark k^I, calculated according to the pyridine N-oxide decrease; the blackened points were calculated according to the accumulation of its hydrochloride salt.

Applying the principle of quasistationary concetration in case of the intermediate particles Ia and Ib, the following expression for the observed pseudofirst order rate constant k^I can be obtained (if [DPCP] $\gg$ B]):

$$k^I = \frac{k_1(k_2k_4 + k_3k_{-2}[Cl^-] + k_3k_4[NuH])[DPCP][NuH]}{k_{-2}[Cl^-](k_{-1} + k_3[NuH]) + k_4[NuH](k_{-1}+k_2+k_3[NuH])} \quad (5)$$

or
$$k^I = k'[DPCP][NuH], \quad (6)$$

where k' is a complex function from the concentrations of nucleophilic reagent and chloride anion.

In case of concentrational conditions [DPCP] $\ll$ [B], expression (7), analogous to Eq. (6) is obtained:

$$k^I = k'[B][NuH] \quad (7)$$

Simplified boundary versions of dependences (6) and (7) are also possible. In the low concentration range of the nucleophile, especially in the case of a weakly basic one (e. g., in the case of water in "dry" acetonitrile), inequalities $k_{-2}[Cl^-] \gg k_4[NuH]$ and $k_{-1} \gg k_3[NuH]$ may be valid. Then Eqs. (6) and (7) take the following form (the k' value has been taken into consideration):

$$k^I = \left(\frac{k_1 k_2 k_4}{k_{-1} k_{-2} (Cl^-)} + \frac{k_1 k_3}{k_{-1}} \right) [NuH][DPCP] \quad (\text{if } [DPCP] \ll [B]), \quad (8)$$

$$k^I = \left(\frac{k_1 k_2 k_4}{k_{-1} k_{-2} (Cl^-)} + \frac{k_1 k_3}{k_{-1}} \right) [NuH][B] \quad (\text{if } [DPCP] \ll [B]), \quad (9)$$

Another extreme possibility is a situation when $k_{-2}[Cl] \gg k_4[NuH]$ and $k_{-1} \gg k_3[NuH]$. In this case the expressions for k^I lead to the simplest form :

$$k^I = k_1[DPCP] \quad (\text{if } [DPCP] \gg [B]), \quad (10)$$

$$k^I = k_1[B] \quad (\text{if } [DPCP] \ll [B]), \quad (11)$$

where k_1 ($l \cdot mole^{-1} \cdot s^{-1}$) is the rate constant of the DPCP interaction with pyridine N-oxide.

Thus, Eqs. (5), (7) and their simplified modifications (8)-(11) predict the first order according to the substrate and the catalyst, the variable order according to the nucleophilic reagent, decreasing from one to zero proportionally to the increase of its concentration, as well as the inhibiting action of chloride anion.

The facts illustrating this effect have been given above. These are the decrease of constants k^I in the duration of the process in case of a low nucleophilic concentration (e.g. in acetonitrile, containing the residual moisture, only) and the behavior of the k^I values if the lithium chloride additions are observed (Fig. 1), corresponding to Eqs. (8),(9).

The experimental data concerning the reaction order according to the nucleophile show that in case of the given DPCP concentration, the k^I constants in the range of small nucleophilic additions (water and methanol) grow with the increase of the concentration of the latter (Fig. 3), which qualitatively agrees with Eq. (8). In the concentration range of approximately 0.1-0.3 to 0.7 $mole \cdot l^{-1}$, the k^I val-

ues do not depend either on the nucleophile concentration or its nature (Fig. 3), as it actually follows from Eq. (10). If the concentration of water is more than 0.7 mole·l^{-1}, a decrease of the k^I values can be observed.(see curve 3 in Fig. 3). A similar dependence of the reaction rate on the nucleophile (hydroxide ion) concentration has been noticed in the case of the alkaline hydrolysis of 4-nitrophenyl esters of dialkylic- and diarylphosphoric acids in acetonitrile (the rates of hydrolysis reach their peak values if the water concentration is 0.02-0.3 mole·l^{-1})[15, 16].

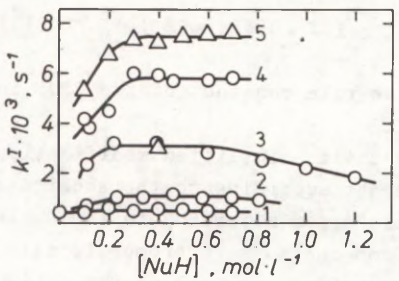


Fig. 3. Dependence of the k^I values on nucleophile concentration (○ - H_2O, Δ - CH_3OH) in hydrolysis and methanolysis reactions of DPCP in acetonitrile, catalyzed by pyridine N-oxide (B); [DPCP] [B], 25°C. [DPCP]·10^3 mole·l^{-1}: 1-0.15 1-0.15; 2-0.34; 3-0.93; 4-1.67; 5-2.39.

The linear ascending regions of the curves in Fig. 3 should obey Eq.(8). Unfortunately, calculation of either the individual rate constants or their algebraic combinations by means of this equation is complicated since it is difficult to experimentally assess accurately enough the chloride-ion concentration, brought to the zero time or zero yield because (cf.[11]) a small amount of it can be introduced in the form of the HCl admixture in the initial DPCP.

The averaged k^I values for the hydrolysis and methanolysis reactions, corresponding to the horizontal regions of the curves in Fig. 3 are presented in Table 2. Owing to a much higher nucleophility of amines, the independence of k^I of their concentration and nature is observed at remarkably

Table 2

Averaged $\bar{k}^{I}$ Values Not Depending on Concentration of Nucleophilic Reagents of Rate Constants for DPCP Hydrolysis, Methanolysis and Aminolysis Reactions Catalyzed by Pyridine N-Oxide in Acetonitrile, 25°C

No	Nucleophile	[NuH] mole·l^{-1}	[DPCP]·10^{3} mole·l^{-1}	[B]·10^{3} mole·l^{-1}	$\bar{k}^{I}$·10^{3}, s^{-1}	N[a]	Methods
1	2	3	4	5	6	7	8
1	Water	≈ 5·10^{-3}	≈ 0.05	0.20	0.83±0.02	1	conduct.
2				0.26	1.09±0.04	1	
3				0.51	2.33±0.06	1	
4				0.82	2.79±0.08	1	
5				1.10	4.53±0.20	1	
6				1.43	5.56±0.04	1	
7				1.73	7.32±0.11	1	
8				2.00	8.37±0.55	1	
9				2.53	10.60±0.20	1	
10		0.06 - 0.53		0.60	2.52±0.13	4	
11		0.12 - 0.70		0.83	3.88±0.18	4	
12		0.45		1.70	6.86±0.11	1	
13		0.10 - 0.70	0.15	≈0.05	0.47±0.02	7	spectr.

Table 2 continued

1	2	3	4	5	6	7	8
14		0.20 - 0.70	0.34		1.07 ± 0.03	5	
15		0.40	0.70		2.36 ± 0.03	1	
16		0.20 - 0.60	0.93		3.07 ± 0.13	3	
17		0.40	1.17		3.71 ± 0.02	1	
18		0.30 - 0.60	1.67		5.81 ± 0.06	5	
19		0.40	2.14		6.36 ± 0.10	1	
20		0.40	2.34		7.04 ± 0.05	1	
21	Methanol	0.40	0.93	≈0.05	$2.97\pm.04$	1	spectr.
22		0.30 - 0.70	2.39		7.46 ± 0.08	5	
23	Diethyl-amine	0.0004	≈0.05	0.09	0.31 ± 0.14^{b}	1	conduct.
24				0.22	0.47 ± 0.13^{b}	1	
25				0.44	1.58 ± 0.14^{b}	1	
26				0.88	3.15 ± 0.15^{b}	1	
27	3-Nitro-	$(0.05\text{-}6)\cdot10^{-3}$		0.31	1.58 ± 0.05	3	conduct.
28	aniline	$(0.10\text{-}10)\cdot10^{-3}$		0.62	2.97 ± 0.10	8	

a - the number of averaged k^{I} values (number of experiments at different concentrations of nucleophile. b - $k^{I} - k^{I}_{o}$ differences are given.

lower concentrations than in case of water and methanol. Therefore, for the aminolysis processes in the concentration range of amines studied, there are no rising regions of the "k^I - [NuH]" dependences. The k^I values given in Table 2 for the aminolysis reaction do not depend on the nucleophile concentration.

Eqs. (8)-(11) show that the reaction orders according to the substrate and catalyst equal unity in the whole range of the concentration change of the nucleophile. The above given (see Fig. 2) linear dependence between the k^I values and [DPCP] for the hydolysis of DPCP in acetonitrile refers to the first reaction order according to the substrate. The first order concerning both the substrate and the catalyst, is retained also in the range of the k^I constants' independence of the nucleophile nature and concentration. This is illustrated by the straight lines in Fig. 4, constructed according to the results of spectrophotometric (straight line I) and conductometric (straight line II) measurements. The averaged $\bar{k}^I$ values for different nucleophiles and various concentrations of one and the same nucleophile are situated on the common straight lines.

The k_1 values calculated as the tangents of the slope curves of straight lines I and II equal 3.03 ± 0.10 and 4.16 ± 0.11 $l \cdot mole^{-1} \cdot s^{-1}$, respectively. These k_1 values, obtained by means of two different techniques are in a satisfactory correspondence.

It can be stated on the basis of the aforesaid that the character of the experimentally found dependences, given in Figs. 1-4 are in good qualitative correlation with (5) or (7). Thus, the kinetic regularities of the DPCP reactions with OH- and NH-nucleophiles catalyzed by pyridine N-oxide in acetonitrile can be described by Scheme (4) of the nucleophilic mechanism of catalysis and therefore prove its validity.

We should also like to draw attention to an important result of this study. In contrast to the analogous catalytic processes of transfer of acyl and arylsulfonyl groups in aprotic media (see[1-3], also[17]) in the case of which it is

under any circumstances impossible to change the rate determining stage (the interaction of the intermediate product of type I with NuH) in the limits of the nucleophilic mechanism, it can easily be done in the reaction studied by means of varying the concentration of even such weak nucleophiles as water or alcohol.

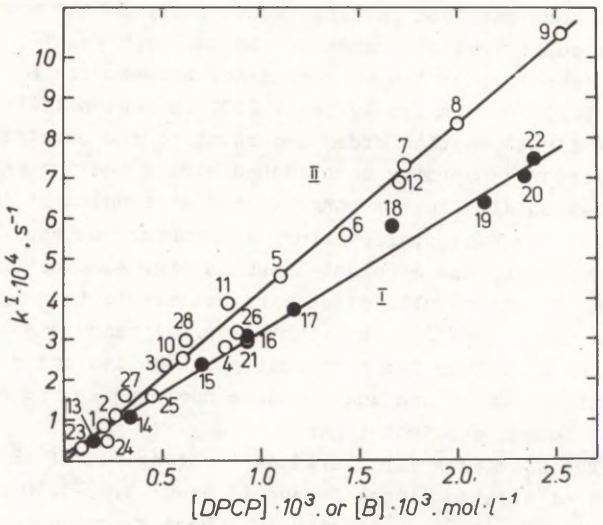


Fig. 4. Dependence of averaged $\bar{k}^I$ constants on the DPCP concentration (I, [DPCP] $\gg$ [B]) and on pyridine N-oxide (II, [DPCP] $\ll$ [B]) in reactions of DPCP with nucleophiles (according to data of Table 2), catalyzed by pyridine N-oxide in acetonitrile at 25°C. Plot numbers correspond to those of Table 2.

Straight line I: $\bar{k}^I = (1.6 \pm 1.6) \cdot 10^{-4} +$
$+ (3.03 \pm 0.10)$ [DPCP],
$s_o = 2.56 \cdot 10^{-4}$, r = 0.995, N = 10.

Straight line II: $\bar{k}^I = -(0.6 \pm 1.2) \cdot 10^{-4} +$
$+ (4.16 \pm 0.11)$ [B],
$s_o = 3.11 \cdot 10^{-4}$, r = 0.995, N = 18

It gives experimental possibilites for systematic studies of the nucleophilic reactivity of pyridine N-oxides as the catalysts of the processes of acyl transfer in aprotic media. This phenomenon has been widely studied[1-3, 18], although the causes of the "abnormally" high nucleophilic reactivity of pyridine N-oxides remain unexplained in several aspects (e.g. see[18]).

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EFFECT OF SODIUM PERCHLORATE ON KINETICS AND REACTION MECHANISM OF HYDROLYSIS AND AMINOLYSIS OF N-ARYLBENZIMIDOYL CHLORIDES IN DIOXANE-WATER (9:1) MIXTURE

L.P. Drizhd, L.I. Bondarenko, M.D. Vdovichenko, and V.A. Savyolova
Institute of Physical Organic Chemistry and Coal Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk

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Interaction kinetics of N-arylbenzimidoyl chlorides with 4-N,N-dimethylaminopyridine and water in dioxane-water (9:1) mixture at 25°C has been studied. The first reaction order of aminolysis according to each reagent, absence of effect of similar ion, increase of rate if electron donor substituent is conducted into substrate molecule are in keeping with the S_N2 (IP) mechanism. Adding sodium perchlorate leads to rate increase with a simultaneous change of rate determining caused by proceeding of the processes via the free nitrilium cation. Accelerating effect of salt will disappear entirely if the 18-crown-6 reaction mixture is added. Supposedly, in case of participation of salt, the $Na^+ClO_4^-$. S_N1 mechanism is realized.

The kinetics of neutral hydrolysis of imidoyl halogenides $R^1C(X)=NR^2$ (X=Hal, R^1=R^2=Alk, Ar) has not been studied very

thoroughly[1,2] yet. The stage mechanism of nucleophilic substitution via the nitrile-cation intermediates (either a free ion or ion pairs) is supposed to operate in case of the process studied. The existence of the mechanism can be confirmed by the following facts: a) the character of the substituent effect on the rate[1,2]; b) the effect of a similar ion[2]; c) accelerating effect of salts which do not contain anions[2]; d) high susceptibility of the reaction rate to the changes of the medium's polarity[2]. As to the molecularity of the rate limiting stage and the reaction form of the nitrile cation intermediate in case of similar compound types in similar media[*], the statements of the authors[1,2] are to a certain extent contradictory. Thus, it is supposed[1] that in the acetone-water mixture (10.9% of water), the hydrolysis rate of diarylimidoyl chlorides can be determined by the water molecules' attack at the nitrilium cationic ion pair, i.e. the S_N2 (IP) mechanism is observed. According to the authors of[2], in the dioxane-water (9:1) mixture having a poorer solvency, the hydrolysis proceeds via the free nitrilium cation, while the ionization of imidoyl chlorides i.e., the S_N1(I) mechanism, is considered to be the rate limiting stage.

These differences seem to result from different conditions of conducting kinetic measurements in the paper cited. In fact, the hydrolysis of diarylimidoyl chlorides in[2] was performed at a constant ionic strength of the solvent caused by the sodium perchlorate effect, while the solvolysis of the same substrates in[1] was carried out without salt additions. It is known that the perchlorate salts remarkably effect the rate of the S_N1 processes at the saturated carbon atom[3]. It is possible that in the case of the hydrolysis of imidoyl chlorides, sodium perchlorate will alter not only the reactive substrate form but also the rate limiting stage. Never-

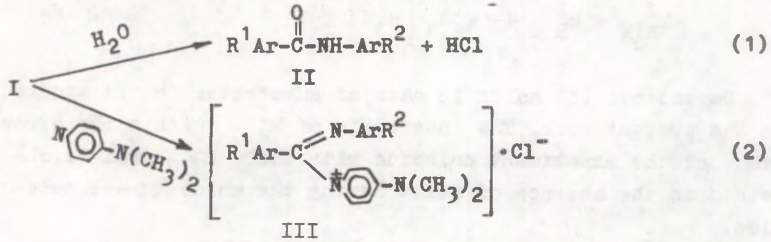
[*] Owing to poor solubility and extremely high hydrolysis rate of imidoyl chlorides in water, the reaction was studied in aqueous-organic mixtures of dioxane[2] and acetone,[1] containing relatively substantial amounts of organic component.

theless, this problem was not specially studied in the papers referred to.

In order to go more deeply into the details of the reaction mechanism, the present report deals with the kinetics and the salt effect on the hydrolysis rate of N-arylbenzimidoyl chlorides $R^1ArC(Cl)=NArR^2$ (I, R^1=H, R^2=4-CH_3, a) H, b) 4-Cl, c) 3-Br, d) in the dioxane-water (9:1) mixture at 25°C.

For the purposes of comparison, the kinetics of reaction of imidoyl-chlorides Ib, Id with 4-N,N-dimethylaminopyridine was studied under the same conditions.

During the hydrolysis of the Ia-d compounds form the corresponding amides II[1,2]. The Ib, Id aminolysis leads to the formation of imidoyl pyridine salts III (cf.[4]), which are[5] quite resistant to the hydrolysis:



(1)

(2)

The IRS analysis of reaction mixtures has shown that in case of the 4-N,N-dimethylaminopyridine concentration exceeding the $8 \cdot 10^{-3}$ mol·l^{-1} the II accumulation is accompanied by the formation of imidoyl-pyridine salts III. The IIIb salt will not practically get hydrolyzed within the duration of the experiment even in case of very large excesses of the tertiary amine. In the same conditions, the IIId salt partially undergoes the hydrolysis, its rate increasing with the increase of the concentration of the pyridine base. In the presence of sodium perchlorate, there is no consumption of the IIId product on the expense of the following solvolysis during kinetic measuring. Decrease of the hydrolysis rate caused by the perchlorate conducted into the system is in good agreement with the earlier obtained data[5] concerning the kinetics of alkaline hydrolysis of imidoyl

pyridine salts III stabilized by various anions, the perchlorate ion included, in the dioxane-water (1:1) medium.

In case of the 4-N,N-dimethylaminopyridine absence, the process rate of the process was monitored according to the accumulation of amide II at 285 nm under pseudomonomolecular conditions $[H_2O] \simeq 5.6$ mol·l^{-1}; $[I] \simeq 10^{-5}$ mol·l^{-1}. The pseudomonomolecular rate constant $k^I_{H_2O}$ corresponds to the process (see below). In case of 4-N,N-dimethylaminopyridine, the rate was monitored according to the formation of salt at 345 nm, the conditions being $[H_2O] \simeq 5.6$ mol·l^{-1} $> [R_3N] \gg [I] \simeq 10^{-5}$ mol·l^{-1}. In this case (cf.[6]), the pseudofirst order rate constant, marked as $k^I_{R_3N}$, describes the total expenditure of substrate I and can be expressed by Equation (3):

$$k^I_{R_3N} = k^I_{H_2O} + k^{II}_{R_3N} [R_3N] \qquad (3)$$

Dependence (3) holds in case of substrates Ib, Id studied in the present work. The intercepts of $k^I_{H_2O}$ within the error range of the experiment coincide with the $k^I_{H_2O}$ values, obtained in the absence of amine during the amide II accumulation.

The $k^{II}_{R_3N}$ constants formally correspond to the bimolecular interaction of I with 4-N,N-dimethylaminopyridine*.

The rate constants of pseudofirst order $k^I_{H_2O}$ and $k^I_{R_3}N$ were calculated as follows:

$$k^I_{H_2O} = \frac{1}{t} \ln \frac{D_\infty - D_o}{D_\infty - D_t} \qquad (4)$$

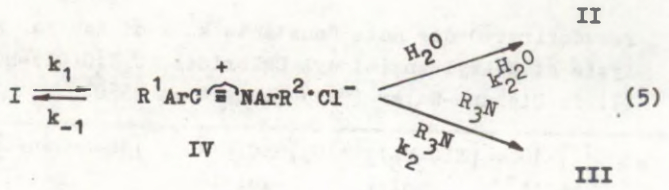
For the Id reactions in the presence of 4-N,N-dimethyl-

* In fact, they can be to a certain extent increased towards to the k_{base} H_2O value, where k_{base} (l^{2}mol^{-2}·s^{-1}) is the rate constant of the basic catalysis of hydrolysis of substrates I with 4-N,N-dimethylaminopyridine. Still, it is not possible to definetely establish it. We did not continue the analysis of the $k^{II}_{R_3N}$ values.

aminopyridine and in the absence of sodium perchlorate the $k^{I}_{R_3N_6}$ values were found applying the Guggenheim methods (see[6]).

Kinetics and Reaction Mechanism in Absence of Sodium Perchlorate.

Peculiarities of Kinetics. Without electrolyte additions ($NaClO_4$), the rate constants of the solvolysis $k^{I}_{H_2O}$ as well as the simultaneous solvolysis and aminolysis of $k^{I}_{R_3N}$ imidoyl chlorides, I remain unchanged during the process, neither depending on the initial concentration of the substrate nor on the chloride salt (NaCl, $N(C_2H_5)_4Cl$) and 18-crown-6 conducted into the reaction mixture (Tables 1,2). Decelarating effect of sodium chloride was not observed if crown ether was added (Table 1). Thus, the effect of a similar anion was not observed in the processes studied. According to the mechanism[1,2] including a preliminary ionization of of the substrate (see Scheme (5)), it means that the contribution of the free nitrilium cation into the total reaction rate is extremely small. The hydrolysis and aminolysis most probably proceed via ion pair IV:



(5)

This assumption can be confirmed especially by the kinetics of formation of imidoyl pyridine salts IIIb, IIId.

Application of the stationarity condition in case of Scheme (5), leads to expression (6) for the studied pseudo-first order rate constant of the aminolysis $k^{I}_{R_3N}$:

$$k^{I}_{R_3N} = \frac{k_1 k_2^{R_3N}[R_3N]}{k_{-1} + k_2^{R_3N}[R_3N]} + \frac{k_1 k_2^{H_2O}[H_2O]}{k_{-1} + k_2^{H_2O}[H_2O]} \qquad (6)$$

As it was already pointed out, the "$k^{I}_{R_3N}$-$[R_3N]$" dependendence for the reaction with participation of the Ib, Id compounds is linear in the studied concentration range of 4-N,N-dimethylaminopyridine. Thus, under the conditions of experiment, holds $k_{-1} > k_2^{R_3N}[R_3N]$. It confirms that for the formation reaction of imidoyl-pyridine salts, the attack of pyridine base at the ion-pair intermediate IV ($k_2^{R_3N}$) can be considered the rate limiting stage in Scheme (5). The same conclusion holds also in case of hydrolysis of imidoyl-chlorides Ia-d. Actually, the parallel (in a number of cases it is predominant) formation of the IIIb and IIId salts in the dioxane-water (9:1) mixture is connected with obeying the $k_2^{R_3N}[R_3N] \gg k_2^{H_2O}[H_2O]$ relationship. Thus, the $k_{-1} > k_2^{H_2O}[H_2O]$ definitely holds in case of solvolysis, i.e., its rate can be determined by the stage of the water attack at the nitrilium cationic ion pair IV. Consequently:

$$k^{I}_{R_3N} = \frac{k_1 k_2^{R_3N}}{k_{-1}}[R_3N] + \frac{k_1 k_2^{H_2O}}{k_{-1}}[H_2O] \qquad (7)$$

Table 1

Pseudofirst Order Rate Constants $k^{I}_{H_2O}$ of Neutral Hydrolysis of N-Arylbenzimidoyl Chlorides $C_6H_5C(Cl)=NC_6H_4R$ (I) in Dioxane-Water (9:1) Mixture at 25°C

R	$[I]\cdot10^5$, mol·l^{-1}	$[N(C_2H_5)_4]\cdot10^3$, mol·l^{-1}	$[NaCl]\cdot10^3$, mol·l^{-1}	[18-crown-6]·10^2, mol·l^{-1}	$k^{I}_{H_2O}\cdot10^3$, s^{-1}
1	2	3	4	5	6
4-CH_3	4.9	-	-	-	3.91
	5.1	-	-	-	3.97
	6.1	-	-	-	3.88

Table 1 continued

1	2	3	4	5	6
	9.8	-	-	-	3.87
	9.8	-	-	-	4.05
			$\bar{k}^{1}_{H_2O}=(3.94 \pm 0.09)\cdot 10^{-3}$		
H	0.9	-	-	-	1.47
	1.8	-	-	-	1.51
	2.7	-	-	-	1.54
	2.7	-	0.686	-	1.41
	2.7	-	1.03	-	1.35
	2.7	-	1.72	-	1.43
	4.2	-	-	-	1.55
	4.2	1.63	-	-	1.44
	4.2	4.07	-	-	1.53
	4.2	8.14	-	-	1.44
	5.0	-	-	-	1.50
	6.1	-	-	1.81	1.43
	6.1	-	-	3.63	1.49
	6.6	-	-	1.81	1.44
			$\bar{k}^{I}_{H_2O} = (1.51\pm0.04)\cdot 10^{-3}$ =		
4-Cl	3.8	-	-	-	0.330
	3.8	-	-	-	0.310
	7.6	-	-	-	0.340
	7.7	-	-	-	0.371
			$\bar{k}^{I}_{H_2O} = (3.36\pm0.31)\cdot 10^{-4}$		
3-Br	4.2	-	-	-	0.145
	4.2	2.04	-	-	0.149
	4.2	1.02	-	-	0.147
	4.2	-	-	-	0.148
	5.2	-	-	-	0.154
	5.4	-	-	-	0.153
	5.5	-	5.0	-	0.147

Table 1 continued

1	2	3	4	5	6
	5.5	-	5.0	1.02	0.151
	5.5	-	5.0	2.03	0.146
	5.5	-	5.0	3.05	0.148
	5.9	-	-	-	0.156

$k^{I}_{H_2O} = (1.52 \pm 0.05) \cdot 10^{-4}$ *

* Mean value of the experiments without salt additions.

Table 2

Rate Constants of Pseudofirst $k^{I}_{R_3N}$ and Second $k^{II}_{R_3N}$ Order of N-Arylbenzimidoyl Chlorides $C_6H_5C(Cl)=NC_6H_4R(I)$ Reaction with 4-N,N-Dimethylaminopyridine in Dioxane-Water (9:1) Mixture at 25°C

R	[18-crown-6]·10² mol·l⁻¹	[NaCl]·10³ mol·l⁻¹	[N(C₂H₅)₄Cl]·10³ mol·l⁻¹	[R₃N]·10² mol·l⁻¹	$k^{I}_{R_3N} \cdot 10^3$ s⁻¹
1	2	3	4	5	6
H	-	-	-	1.71	4.95
	-	-	-	2.05	5.41
	-	0.686	-	2.05	5.49
	-	1.03	-	2.05	5.56
	-	1.73	-	2.05	5.56
	-	-	-	2.19	5.47
	-	-	-	2.82	6.77
	-	-	-	4.13	9.02
	-	-	-	6.29	12.6
	-	-	-	8.25	16.4
	-	-	-	12.8	24.0
	-	-	-	26.3	43.6

Table 2 continued

1	2	3	4	5	6
H	-	-	2.75	1.71	5.34
			5.50	1.71	5.31
		$k^{II}_{R_3N}$ = (15.9±0.3)·10^2 l·$mol^{-1}s^{-1}$ *			
3-Br	-	-	--	0.892	0.170
				1.08	0.185
	2.75	-	-	1.08	0.190
	8.25	-	-	1.08	0.172
	13.8	-	-	1.08	0.199
	55.0	-	-	1.08	0.199
	-	-	-	1.78	0.269
	-	-	-	2.23	0.326
	-	-	-	3.37	0.484
	-	-	2.75	3.37	0.492
	-	-	5.50	3.37	0.492
	-	-	-	5.01	0.606
	-	-	-	6.48	0.751
	-	-	-	7.85	0.950
	-	-	-	10.1	1.18
	-	-	-	11.8	1.43
	-	-	-	13.4	1.58
		$k^{II}_{R_3N}$ = (1.12±0.02)·10^2 l·$mol^{-1}s^{-1}$ *			

* Calculated according to experiments without salt and crown-ether additions.

Facts Confirming Existence of S_N2 (IP) Mechanism.

Although the above data on the kinetics of the hydrolysis and aminolysis of the Ia-d imidoyl chlorides and the absence of the effects of chloride salts on their rate are in correspondence with the S_N2(IP) mechanism, the results do not contradict the mechanism of bimolecular substitution. According to the latter, the attack of nucleophilic agents can be directed at the covalent substrate I, and not at ion pair IV

of the S_N2 (S) process. The data concerning the substituent effect on the reaction rate in the imidoyl molecule permit to exclude the alternative, as it was demonstrated on the example of the aminolysis processes of analogous substrates in chloromethylene[7].

For the hydrolysis rate constant ($k^I_{H_2O}$) of the Ia-d imidoyl chlorides, holds the Hammett dependence (8):

$$\log k^I_{H_2O} = -(2.81\pm0.02) - (2.61\pm0.08)\sigma_R2 \qquad (8)$$

$$N = 4;\ s_o = 3.42\cdot10^{-2};\ r = 0.999$$

A relatively high negative value of ρ_R2, which equals -2.61 in case of the reaction studied, clearly evidences about the ion-pair mechanism, given in Scheme (5).The value is close to that obtained earlier in[2] ($\rho_R2 = -2.75$) for the same reaction series in the presence of 0.01 M $NaClO_4$ and the $\rho_R2 = -2.3$[7] for the aminolysis of compounds I in chloromethylene, in whose case the S_N2(IP) mechanism is also postulated. It should be stressed that for the S_N2 (S) processes with participation of imidoyl chlorides I, in aprotic media the ρ_R2 parameters differ from those obtained by us by their absolute values and signs. Thus, in case of the bimolecular interaction of N-arylbenzimidoyl chlorides I with 4-N,N-dimethyl aminopyridine in chloromethylene $\rho_R2 = +2.3$[7] but in acetonitrile $\rho_R2 = +1.77$[4].

At the same time, the ρ_R2 values obtained in the present work, remarkably differ from the analogous parameter of the ionization process (k_1) of compounds I in acetonitrile ($\rho_R2 = -5.0$[4]). This phenomenon can be easily explained, since in the case of the S_N2 (IP) mechanism (Scheme (5), kinetic equation (7)), the ρ_R2 value is a complex one and reflects not only the susceptibility to the substituents' induction effect of the ionization stage of the substrate (k_1) but also that of the following stages of the ion pair transformation (k_{-1}, k_2):

$$\rho_R2 = \rho_1 + \rho_2 - \rho_{-1} \qquad (9)$$

The data about the selectivity of the process concerning the nucleophiles studied, i.e. water and 4-N,N-dimethylaminopyridine do not contradict the ion pair mechanism of these reactions. Assuming that in case of both the hydrolysis and aminolysis reactions holds the first reaction order according to nucleophile, it can be said on the bases of the observed rate constants given in Tables 1,3, taking also into consideration the concentrations of water in the mixture (5.6 mole·l^{-1}) and the rate equation (7) for substrates Ib, Id that the selectivity values S equal:

$$S_{IIb} = \frac{k_2^{R_3N}}{k_2^{H_2O}} = 589 \pm 27$$

$$S_{IId} = \frac{k_2^{R_3N}}{k_2^{H_2O}} = 415 \pm 21$$

It can be said on the basis of the results that the stage of transformation of intermediates IV into the final products is quite susceptible to the attacking nucleophile nature. If the nitrilium cation becomes more stable, the reaction selectivity of the ion pair also tends to increase: IVd < IV b. Nevertheless, it is hard to say, whether it is a general tendency for all substrates of type I.

Kinetics and Reaction Mechanism in Presence of Sodium Perchlorate

Kinetic Regularities. Adding sodium perchlorate into the reaction mixture leads to a remarkable acceleration of the hydrolysis and aminolysis of imidoyl chlorides I. In presence of salt and in case of the correlation of the reagents $[H_2O] > [R_3N] > [I] \simeq 10^{-5}$ mole·l^{-1}, the pseudofirst order rate constants of hydrolysis ($k^c_{H_2O}$) and aminolysis ($k^c_{R_3N}$), calculated by means of Eq. (4), remain the same during the reaction. Their values are given in Tables 3,4.

Tables 3,4 show that in case of fixed concentrations of sodium perchlorate, the accumulation rates of both amide II and salt III are quite close for substrates Ib and Id, not depending on the 4-N,N-dimethylaminopyridine concentration in the solution. Thus, in the presence of sodium perchlorate, the attack of nucleophilic reagents at the nitrilium cation ion pair cannot be the rate limiting stage of the both processes (as it was in case of absence of salt).

Table 3

Effect of 18-Crown-6 and Salts on Hydrolysis Rate of N-Arylimidoyl Chlorides $C_6H_5C(Cl)=NC_6H_4R$ (I) in Dioxane-Water (9:1 volume) Mixture at 25°C

R	(18-crown-6)·10^3 mole·l^{-1}	($NaClO_4$)·10^3 mol·l^{-1}	(NaCl)·10^3, mol·l^{-1}	$k^c_{H_2O}$, $s^{-1}\cdot10^4$	$(k^c_{H_2O}-k^I_{H_2O})$, s^{-1}
1	2	3	4	5	6
H	-	1.04	-	123	108
	-	1.11	-	174	159
	-	2.50	-	340	325
	18.1	2.50	-	159	144
	-	3.32	-	423	408
	-	4.00	-	515	500
	-	5.32	-	657	642
	18.1	5.32	-	253	238
			k_c = (12.1±0.5) $l\cdot mol^{-1}s^{-1}$ *		
3-Br	-	0.992	-	6.42	4.91
	6.51	0.992	-	1.45	~0
	12.2	0.992	-	1.54	~0
	27.1	0.992	-	1.53	~0
	-	2.24	-	13.5	12.0
	-	3.11	-	16.1	14.6
	-	3.35	-	19.4	17.9
	-	4.11	-	22.8	21.3
	-	5.00	-	28.6	27.1

Table 3 continued

1	2	3	4	5	6
	-	5.00	0.200	18.0	16.5
	-	5.00	0.380	13.4	11.9
	-	5.00	0.750	10.0	8.50
	-	5.00	1.00	8.53	7.02
	-	5.00	1.25	7.38	5.87
	-	5.00	2.10	4.95	3.44
	-	5.00	2.50	4.50	2.99
	-	5.00	3.75	3.08	1.57
	-	5.00	4.50	2.82	1.31
3-Br	-	5.00	5.00	3.06	1.55
	-	5.59	-	29.3	27.8
	-	7.06	-	35.8	34.3
	-	10.0	-	51.1	49.6
	-	10.0	-	51.7	50.2
		$k_c = (4.93 \pm 0.11)\cdot 10^{-1}$		$l\cdot mol^{-1}s^{-1}$	*)

* Calculated from the experiments without sodium chlorate and crown-ether additions.

Table 4

Effect of 18-Crown-6 and Sodium Perchlorate on Aminolysis Rate of N-Arylbenzimidoyl Chlorides $C_6H_5C(Cl)=NC_6H_4R$ (I) in Dioxane-Water (9:1 volume) Mixture at 25°C

R	(18-crown-6)·$\cdot 10^3$, mole·l^{-1}	($NaClO_4$)·10^3 mol·l^{-1}	(R_3N)·10^2 mol·l^{-1}	$k^c_{R_3N}\cdot 10^4$, s^{-1}	($k^c_{R_3N}$ - $k^I_{R_3N}$)·$\cdot 10^4 s^{-1}$
1	2	3	4	5	6
H	-	0.223	0.848	69.7	41.1
	-	0.223	1.07	73.9	41.8
	-	0.223	1.48	80.7	42.1
	-	0.446	1.07	109	76.9
	-				

Table 4 continued

1	2	3	4	5	6
	-	0.670	1.07	152	120
	-	1.04	0.982	207	176
	-	1.04	1.74	223	188
	-	1.04	3.05	246	182
	-	1.12	1.07	220	187
	-	1.79	1.07	355	322
	-	2.23	1.07	424	392
	-	3.35	1.07	607	575
		$k_c = (17.2 \pm 0.2)$ l·mole^{-1} s^{-1} *			
3-Br	-	0.75	1.78	5.91	2.41
	-	1.86	1.78	11.9	8.40
	-	3.73	1.78	20.8	17.3
	-	4.10	0.69	23.0	20.7
	-	4.10	0.81	23.9	21.5
	-	4.10	1.01	25.1	22.4
	-	4.10	1.78	23.9	20.4
	-	5.59	1.78	30.9	27.4
	-	7.45	1.78	41.1	37.6
	-	10.0	1.01	55.0	51.5
	-	10.0	2.50	56.8	52.5
	-	10.0	5.34	58.2	51.5
	-	10.0	8.00	61.2	50.7
	-	1.49	1.08	10.9	8.17
	0.69	1.49	1.08	9.23	6.50
	1.38	1.49	1.08	8.23	5.50
	2.75	1.49	1.08	6.88	4.15
	8.26	1.49	1.08	6.34	3.61
	27.5	1.49	1.08	6.19	3.46
	41.3	1.49	1.08	5.93	3.20
		$k_c = (5.23 \pm 0.08) \cdot 10^{-1}$ l·mole^{-1}s^{-1} *			

* Calculated from the experiments without crown-ether additions.

Dependences "$k^c_{R_3N}$ - $(NaClO_4)$" and "$k^c_{H_2O}$ - $(NaClO_4)$" are linear in the studied variation range of the salt concentration, on one hand, evidencing about the absence of a special salt effect caused by varied behavior of salt affecting the contact and solvationally divided ion pairs[8], and on the other hand, referring to the activity of various forms of salt-ion pairs and free cations.

Thus, in the presence of sodium perchlorate, the reaction rate (1,2) can be described by Eqs.(10,11), where $k^I_{H_2O}$ and $k^I R_3N$ are the effective rate constants in the absence of salt but k_c ($l \cdot mole^{-1} s^{-1}$) is the catalytic rate constant, conditioned by the salt molecule action.

$$k^c_{R_3N} = k^I_{R_3N} + k_c(NaClO_4) \qquad (10)$$

$$k^c_{H_2O} = k^I_{H_2O} + k_c(NaClO_4) \qquad (11)$$

The k_c values (Tables 3,4) for the hydrolysis and aminolysis reactions of imidoyl chlorides 1b, Id are fairly close.

It can be seen from Tables 1 and 2 that adding 18-crown-6 (up to 0.05 $mole \cdot l^{-1}$ concentration) does not remarkably affect the rate of the processes studied. At the same time, crown-ether considerably weakens the accelerating effect of perchlorate salt up to its total suppression in case of hydrolysis . It has already been mentioned that sodium chloride affects neither the hydrolysis nor the aminolysis rates both in case of absence or participation of crown ether (Tables 1,2). However, at fixed concentrations of sodium perchlorate, its chloride has a remarkably decelerating effect (Table 4).

Mechanism of Salt Effect

The sodium perchlorate effect on the rate of the reactions studied can be explained by the specific salt effect, since the other salts (NaCl, $N(C_2H_5)_4Cl$) are practically indifferent under such conditions. Its effect can be confirmed by a series of facts:

a) change of the reaction order concerning the nucleophilic reagent (the rate determining stage changes);

b) participation of the cation of salt in the transition state of the rate limiting stage;

c) appearance of a new reactive nitrile-cation substrate form on the reaction coordinate.

The first conclusion must be right, since it is confirmed experimentally by the absence of the dependence of the reaction rate constant k_c on the nucleophile (tertiary amine) concentration and on its nature.

The second conclusion has been drawn on the bases of the data concerning 18-crown-6 effect on the sodium perchlorate, which at the sufficient 18-crown-6 concentration in the reaction mixture totally disappears. These results permit to exclude the ion-pair type reaction mechanism, where in the rate limiting stage the contact ion pair transfers into the solvationally divided one (cf.[9]). Here the accelerating effect of the salt would be caused by a simple chloride-ion exchange in ion pair IV by the perchlorate anion taken without the contribution of the sodium cation. If such an effect was responsible for the sodium perchlorate effect, the increase of the anion concentration at adding crown-ether to salt would lead to the increase of the rate, or at least it would not change it. In fact, a contrary effect has been observed.

It proceeds from obeying the linear dependences (10,11) for the hydrolysis and aminolysis reactions of imidoyl chlorides I that the degrees of the activation of both the free salt cations and its ion pairs* are quite similar. Consequently, in the transition state of the rate limiting stage can participate either the salt cation itself or its ion pair. Evidently, the metal cation contributes electrophilically to the C-Cl bond heterolysis in the imidoyl chloride molecule.

* The data on the state of the NaX salts (X=Cl, Br, ClO_4) in the dioxane-water (9:1) mixture ($\mathcal{E}$ =5.75) will also be published soon.

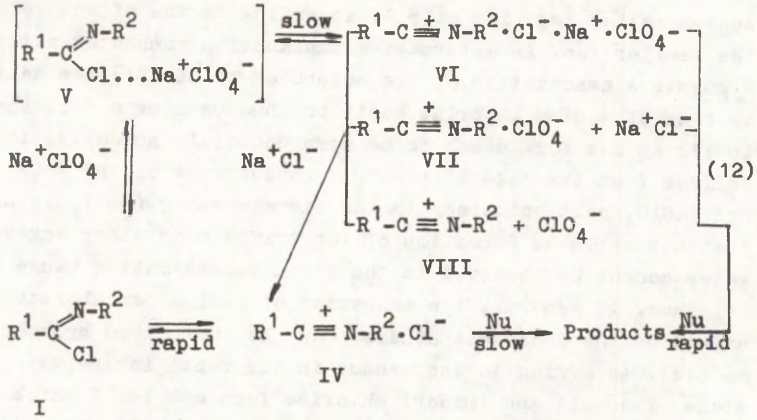
During the ionization process and the following transformations, a more reactive nitrile-cation substrate is formed in the system, if compared with the IV intermediate, e.g. with a free nitrilium cation. Inhibiting action of sodium chloride against the background of perchlorate salt refers to the appearance of the free nitrilium-cation on the reaction coordinate. The character of the "$k^{c}_{H_2O}$ - [NaCl]" dependence for the studied hydrolysis reaction is analogous to that of aminolysis of imidoyl chlorides in acetonitrile in participation of NaCl[4], in the case of which the salt's decelerating action is connected with the return of the free sodium cation into ion pair IV according to the effect of the similar ion. An alternative explanation connected with a possible association of the molecules of perchlorate salt in case of sodium chloride addition thus causing a decrease in its active form seems to be more doubtful. Actually, it follows from the date of electric conductance of the NaCl and $NaClO_4$ salt solutions in the dioxane-water (9:1) mixture that a remarkable formation of ion triplets or other aggregates cannot be observed in the given concentration range.

Thus, in general, the mechanism of sodium perchlorate effect on the processes studied can be described by scheme (12). According to the scheme in the rapid inversive stage, the salt and imidoyl chloride form complex V which slowly transforms via the corresponding aggregates VI, VII into the free nitrilium cation VIII. Formation of final products from aggregates VI-VIII because of the action of nucleophilic agents as well as the mutual transition from VI to VII proceeds during rapid stages, not limiting the rate. In addition to the function of the salt cation in accelerating the ionization of imidoyl chlorides, the peculiarity of scheme (12) is in the absence of the external return of cation V··VIII into ion pair VII being affected by the perchlorate ion. Such a return predominates in the case of chloride ion, i.e. the dissociation of IV cannot proceed up to the free cation without sodium perchlorate participation.

It follows from the aforesaid that in the reactions

studied, sodium perchlorate has a double function. On the one hand, it favors the imidoyl chloride ionization at the expense of the electrophilic contribution of the cation (the rate limiting stage); on the other hand, it excludes the possibility of return into the ion pair and thus into the perchlorate substrate, which, evidently cannot actually take place. Thus, the data obtained by us will characterize the transition from the $S_N2(IP)$ mechanism to the $Na^+ClO_4^- \cdot S_N1$ mechanism in the series of imidoyl halogenides.

These results help also explain the literature data[1,2] available.



The conclusion of the authors of[1] that the hydrolysis of imidoyl chlorides proceeds according to the $S_N2(IP)$ mechanism is valid, since the experiment was carried out without the presence of salt additions. The authors of report[2] are also correct claiming that in case of a constant ion strength supported by sodium perchlorate, the hydrolysis of diarylimidoyl chlorides goes according to the S_N1 mechanism. Thus, taking into consideration the fact that sodium perchlorate can affect the rate limiting stage eliminates the seeming contradictions in interpretation of the results of papers[1,2].

Experimental

N-arylbenzimidoyl chloride was synthesized from the corresponding amides and purified by a double redistillation in vacuum. Sodium perchlorate and sodium chloride of "chemically pure" grade were used without an additional purification. Tetraethylammonium chloride of "pure" grade was reprecipitated with ester from the solution in chloromethylene. Before use, the salts were dried in vacuum (0.1 Torr). 4-N,N-dimethyl aminopyridine was obtained applying known methods[8] and it was twice sublimated in vacuum. Dioxane was purified by means of ordinary technique[9]. Bidistilled water was degasified by boiling it for two hours. The dioxane-water (9:1) mixture was prepared at 20°C, pH of it being 7.15. The solutions of salts and reagents were made by weight.

Kinetic measurements were carried out applying traditional methods. The working solution of 2.5 ml volume, thermostated in a cell was added 0.02 ml of imidoyl chloride solution in toluene at the traditional concentration ($\sim 10^{-3}$ mol·l^{-1}). The mixture was stirred and the cell was put into the thermostated cell of a spectrophotometer SF-46. The error of calculation of the constant from a single experiment according to (3) did not exceed 2%.

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Organic Reactivity
Vol. 24 2(86) 1987

STUDY OF S_N1 REACTIONS USING VERDAZYLS
VIII.* Ph_2CHBr HETEROLYSIS KINETICS IN CYCLOHEXANONE AND ACETOPHENONE. SOLVENT INFLUENCE ON PERCHLORATE CATALYTIC EFFECT

T.L. Pervishko, E.A. Ponomareva, and G.F. Dvorko

Kiev Polytechnical Institute, Chair of Organic Chemistry and Organic Substance Processing, 252056, Kiev

Received June 29, 1987

Ph_2CHBr heterolysis kinetics in acetophenone and cyclohexane at $v = k[Ph_2CHBr]$ was studied. $LiClO_4$ additions gave rise to a linear increase in the reaction rate, whereas the halogenides decreased the latter. The mechanism of perchlorate catalytic effect was discussed.

Our earlier papers of this series[1-6] present data on the kinetics and mechanism of Ph_2CHBr heterolysis in MeCN, $PhNO_2$, 1,2-dichloroethane, propylene carbonate and acetone. In all solvents, excluding acetone[6] special salt effect of perchlorate is observed - the curve of reaction rate constant vs. salt concentration shows a sharp deflection, i.e. the first part of the curve demonstrates rather pronounced increase of the rate constant value with increasing perchlorate concentration and then follows a less steep curve section. In acetone solution such a deflection is missing - here the linear increase of the reaction rate constant with increasing perchlorate concentration is observed. This salt effect is described by Winstein's equation (1)[7]

$$k_s = k(1 + b[M^+ClO_4^-]), \qquad (1)$$

*VII is reported in [1].

where k_s and k are reaction rate constants with and without salt, respectively, and b is a value showing the addition efficiency. Special salt effect may be described by two values of b[1,3-6]. Special salt effect was caused by the catalytic action of the perchlorate anion at the stage of charge separation in an intimate ion pair through the formation of the anion triplet ClO_4^- | solv | R^+X^- [3,6]. Earlier it was suggested[1-6] that this process resulted in the formation of a solvent-separated ion pair, at the present moment, however, it is believed[8-10] that ClO_4^- catalyzed the formation of a space-separated ion pair during the transition of the intimate ion pair nucleofuge to a solvent structural defect, e.g., to a cavity. The solvent-separated ion pair is formed in the following rapid stage.

The special salt effect is an example of the nucleophilic catalysis. Dannenberg[11,12] also connects the special salt effect with the catalytic action of ClO_4^-, suggesting that the perchlorate anion substituted the solvent molecule solvatizing the covalent substrate from the rear side of it. We believe this substitution to occur in the intimate ion pair, i.e. the perchlorate salt effect is determined by the following reactions

$$\text{Solv,Solv}|R^+X^- \overset{ClO_4^-}{\rightleftharpoons} ClO_4^-|\text{Solv}|R^+X^- \longrightarrow ClO_4^-|\text{Solv}|R^+\ldots X^- \quad (2)$$

If an ion triplet is formed, the solvent molecule in the second solvate shell will be substituted since ClO_4^- is unable to form an intimate ion pair with such a stable carbocation as Ph_2CH^+.

The fact that the special salt effect is missing in acetone may be explained by the shift of the equilibrium to the left (2) in this solvent, whereas the special salt effect requires an almost complete conversion of an intimate ion pair into an anion triplet. The matter is that acetone may form stable solvates with the incipient carbocation[13] due to C=O group. To substantiate this suggestion, we studied the Ph_2CHBr heterolysis kinetics in other ketones (PhCOMe, cyclohexanone) as well. Besides, the influence of perchlorate on the rate of the above reactions was also studied.

Kinetic tests were performed as it was reported in[1-6], using triphenyl verdazyl as an internal indicator. The concentrations of the substrate and verdazyl in the tests were 0.15-0.05 mole/l and $1.5 \cdot 10^{-4}$ mole/l, respectively. The reaction was discontinued after 20 to 50 % consumption of the indicator; the substrate conversion degree was 0.05-0.01 %. In all cases involved (with and without salt additions) the reaction rate was fairly well described by the first order kinetic equation.

$$v = k [Ph_2CHBr] .$$

Verdazyl concentration has no influence on the reaction rate. Consequently, similarly to the behavior in other solvents[1-6] verdazyl gets involved in the reaction after the rate-determining step.

Kinetic test results are shown in Table 1.

Table 1

Ph_2CHBr Heterolysis Kinetics in Cyclohexanone and Acetophenone in the Presence of Vd$^{\bullet}$.

Solvent	Temperature, °C	$k \cdot 10^8$, s^{-1} [a]	$\Delta H^{\neq}$ kJ/mole	$\Delta S^{\neq}$ J/mol·K
Cyclohexanone	25.0	1.86 ± 0.04	85 ± 1	-109 ± 3
	30.5	3.44 ± 0.17		
	35.0	6.24 ± 0.04		
	40.5	11.0 ± 0.2		
	44.5	15.6 ± 1.4		
PhCOMe	25.0	6.00 ± 0.05	72 ± 1	-123 ± 5
	30.5	10.6 ± 0.1		
	35.2	15.8 ± 0.1		
	40.5	25.8 ± 0.1		
	45.3	41.6 ± 0.4		
Me_2CO	25.0	15.1 [b]	66 [b]	-155 [b]

[a] Average of 2-4 determinations.
[b] As reported in [6].

The last line in Table 1 shows the kinetic parameters of Ph_2CHBr heterolysis in acetone[6]. In the sequence of solvents cyclohexanone-acetophenone-acetone the reaction rate increases almost by an order of magnitude. This is determined by the decreasing value of $\Delta H^{\neq}$, which makes up for the decrease of $\Delta S^{\neq}$ value in the same solvent sequence.

Table 2 shows the effect of salts on Ph_2CHBr heterolysis in acetophenone and cyclohexanone.

Table 2

The Effect of Salt Additions on Ph_2CHBr Heterolysis Rate in Cyclohexanone and PhCOMe, 25°C

Solvent	Salt; c $\cdot 10^2$, mole/l	k $\cdot 10^8$, s^{-1}
PhCOMe	$LiClO_4$; 0.988	10.9 ± 0.1
	$LiClO_4$; 1.42	13.9 ± 0.2
	$LiClO_4$; 2.63	19.8 ± 0.1
	$LiClO_4$; 2.62	19.8* ± 0.2
	$LiClO_4$; 3.66	23.1 ± 0.1
	$LiClO_4$; 5.25	29.6 ± 0.1
	$Et_4N^+Cl^-$; 0.145	2.90 ± 0.06
Cyclohexanone	$LiClO_4$; 1.01	2.24 ± 0.01
	$LiClO_4$; 2.38	2.58 ± 0.12
	$LiClO_4$; 2.55	2.88 ± 0.10
	$LiClO_4$; 3.96	3.42 ± 0.07
	$LiClO_4$; 5.38	3.70 ± 0.08
	$Et_4N^+Br^-$; 0.0555	1.03 ± 0.01
	$Et_4N^+Cl^-$; 0.10	1.00 ± 0.01

*In the presence of 0.0328 mole/l 18-crown-6.

The halogenides decrease the reaction rate, whereas in the presence of $LiClO_4$ it shows linear increase with increasing salt concentration. Special salt effect is not observed. The pattern of salt effects is similar to that in acetone solution[6]. The addition of dibenzo-18-crown-6 has no effect on the reaction rate as in MeCN[5] solution. This speaks for

the fact that the perchlorate effect has no relation to Li^+ catalytic action similar to that observed in 1-adamantyl-p-toluene sulfonate[14]. Active agents in the perchlorate solution may be either the anion ClO_4^- or the salt ion pair. As reported in [15], these agents are of equal catalytic effect thus explaining the linear increase of rate constant with increasing perchlorate concentration.

Table 3 shows the comparison between the log values for Ph_2CHBr heterolysis rate in three ketons as well in MeCN, PhCN and 1,2-dichlorethane, on the one hand, and b-parameter values [Equation (1)] and several other solvent parameters, on the other hand. In the last three solvents, where special salt effect is observed the b value is taken for the first part of the curve $k - [M^+ClO_4^-]$.

Table 3

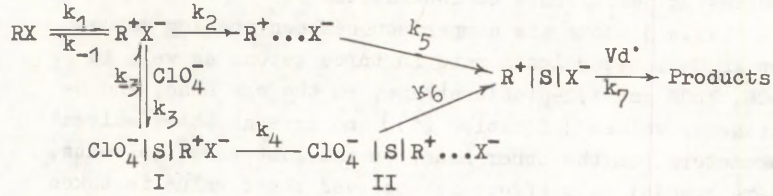
The Effect of Solvent Nature on Ph_2CHBr Heterolysis Rate and on Perchlorate Salt Effect Value, 25°C

Solvent	$-lgk_{25}$	b		Z, kcal/mole	$\varepsilon(20)$	B, cm^{-1}
		$LiClO_4$	Et_4NClO_4			
Cyclohexanone	7.73	19.0±0.1	-	64.8	18.3	242
Me_2CO	6.85	37.8±0.1	3.2±0.1	65.7	20.7	224
PhCOMe	7.22	69.4±0.1	-	65.4	17.4	202
MeCN	5.60	69.3±0.1	48.7±0.1	71.3	37.5	160
PhCN	7.49	860.2±0.1	208.5±0.2	65.0	25.2	155
1,2-dichloroethane	7.83	-	705.7±0.1	63.4	10.4	40

Positive salt effect during organic substrate heterolysis is usually considered to increase with decreasing solvent polarity[16]. In our case we deal with special salt effect rather than that of ion force. The value of the former described by b-parameter shows no correlation (see Table 3) with the solvent polarity parameters ε and Z (Kosower parameter[17]). The above table shows b-values to grow with the

decreasing nucleophilic level of the medium (B-parameter[18]) both for $LiClO_4$ and $Et_4N^+ClO_4^-$. The second peculiarity of the perchlorate effect lies in the fact that $LiClO_4$ gives a much greater increase in the reaction rate than $Et_4N^+ClO_4^-$.

Ph_2CHBr heterolysis mechanism in the presence of Vd• and perchlorate may be written as



Without perchlorate additions the reaction rate is determined by the step of converting the intimate ion pair into the space-separated one (k_2), which then is rapidly transformed into the solvent-separated ion pair (k_5) and the latter shows a fast reaction with Vd• (k_7). In the presence of perchlorate an ion triplet (I) is formed and then slowly converted into a triplet with a space-separated ion pair (II), the latter triplet in its turn is quite rapidly transformed into a solvent-separated ion pair (k_6). Reverse reaction from solvent-separated and space separated ion pairs seems to have no considerable importance[3,10]. Thus, the reaction in the presence of perchlorate goes along two paths, its rate being

$$v = k_2[R^+X^-] + k_4[ClO_4^-|S|R^+X^-],$$

where $$[R^+X^-] = \frac{k_1(k_{-3} + k_4)\,[RX]}{(k_{-1} + k_2 + k_3[ClO_4^-])(k_{-3}+k_4) - k_3 \cdot k_3[ClO_4^-]},$$

and $$[ClO_4^- |S| R^+X^-] = \frac{k_3[R^+X^-][ClO_4^-]}{k_{-3} + k_4}.$$

With increasing perchlorate concentration the concentration of the intimate ion pair visibly decreases, whereas that of the anion triplet goes up. Under the rate-determining formation of space-separated ion pairs (i.e. $k_2 \ll k_{-1}$ and

$k_4 \ll k_{-3}$ with the increase of perchlorate concentration, when $R^+X^- \rightleftharpoons ClO_4^-|S|R^+X^-$ equilibrium is almost entirely shifted to the tight should tend to a constant value $k = \frac{k_1 \cdot k_4}{k_{-1}}$. Therefore, the catalytic effect of the perchlorate should have the form of a saturation curve. This is shown fairly well in a propylene carbonate solution[1], where the usual salt effect is practically of no value. In less polar solvents (PhCN, MeCN, $PhNO_2$, 1,2-dichloroethane) the nucleophilic catalytic effect of perchlorate is superimposed by the usual salt effect which results in a typical pattern of the special salt effect.

Decreasing perchlorate catalytic effect with the increase in the solvent nucleophility seems to be related to the equilibrium (2) shifting to the left side. A smaller $Et_4N^+ClO_4^-$ effect as compared with that of $LiClO_4$ seems to be determined by the equilibrium $Et_4N^+ + R^+X^- \rightleftharpoons R^+X^-|S| + NEt_4$[3] which is observed in the first case and decreases the $ClO_4^-|S|R^+X^-$ concentration.

Negative salt effects of halogenides both with a common and a non-common anion show that during the Ph_2CHBr heterolysis in ketones no free carbocation is formed. Decreasing the reaction rate in the presence of halogenides seems to be determined by the reaction of the halogen-anion with the space-separated ion pair transforming into the intimate one[10] which later is closed to form a covalent product.

Experimental

The reagents were obtained and purified as reported earlier[2,6]. Cyclohexanone was dried twice with Na_2SO_4 and rectified, b.p. 155°C. Acetophenone was dried twice with K_2CO_3 and rectified three times under vacuum, b.p. 55°C (2-3 Torr). Kinetic tests were performed in the thermostatic cell of SF-18. The reaction rate was controlled against the Vd· consumption. Individual tests showed that the rate control against the verdazylium bromide formation gave fair reproducibility.

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Organic Reactivity
Vol. 24 2(86) 1987

KINETICS OF PHOSGENE SOLVOLYSIS IN ALIPHATIC ALCOHOLS

A.L. Sidelkovskii, S.I. Orlov, L.N. Margolin,
A.F. Vasilev, and A.L. Chimishkyan

All Union Research Institute of Plant Protecting Chemicals,
Moscow, 109088
Moscow D.I. Mendeleev Institute of Chemical Engineering,
Moscow, GSP 125820

Received September 22, 1987

Kinetics of phosgene solvolysis in ROH alcohols (R = Me, Et, n-Pr, n-Bu, s-Bu) in the range of -77 - 0° has been investigated. The effect of substituent structure in alcohol on the reaction rate has been described by E_s^o and n_H constants. The latter parameter characterizes the differences observed in alcohols behavior during alcoholysis and divides them into three groups: methanol, primary alcohols except methanol, and secondary alcohols. The reaction series is shown to be isoentropic and the dependence, describing the influence of both structural factors and temperature on reaction rate, has been found.

Investigation of kinetics of acyl chlorides solvolysis in alcohol is of great interest as in this case alcohols act as reagents and medium at the same time. Out of all acids of chloroanhydrides, phosgene is the least studied in this re-

spect because of its high reactivity. In the only paper devoted to this problem some data on phosgene solvolysis in 2-propanol and 2-butanol are available, but rather a narrow range of temperatures was considered[1]. Thus, it seemed expedient to study the kinetics of phosgene solvolysis in a number of primary and secondary alcohols (reaction (1)) in an expanded temperature range.

$$COCl_2 + ROH \xrightarrow{k} RO-\overset{\overset{O}{\|}}{C}-Cl + HCl \qquad (1)$$

Kinetic measurements were made by the conductometry method, the results are presented in the Table and in Fig.1 through the Arrhenius dependencies.

Table

Rate Constants and Activation Parameters of Phosgene Solvolysis in ROH Alcohols

R	T, °C	k_1, s^{-1}	$10^3 k_2$, $l \cdot mol^{-1} \cdot s^{-1}$	$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J/mol·K
1	2	3	4	5	6
Me	-76.5	0.0328	1.09	36.6±0.8	113 ± 4
	-73.9	0.0445	1.48		
	-73.6	0.0503	1.68		
	-71.2	0.0496	1.66		
	-71.0	0.0551	1.84		
	-71.0	0.0489	1.64		
	-62.3	0.167	5.68		
	-62.0	0.123	4.19		
	-61.0	0.151	5.15		
	-59.5	0.177	6.06		
	-59.5	0.196	6.72		
	-56.0	0.261	8.99		
	-55.5	0.292	10.1		
	-50.0	0.430	15.0		
	-49.5	0.515	18.0		
	-49.0	0.492	17.2		
	-45.2	0.562	19.8		

Table continued

1	2	3	4	5	6
	-41.0	0.950	33.8		
	-40.8	1.15	41.0		
	-39.0	1.38	49.2		
	-38.2	1.34	48.0		
	-37.5	1.46	52.4		
Et	-72.0	0.0328	1.74	30.5±0.7	143 ± 3
	-71.0	0.0378	2.01		
	-60.2	0.0879	4.72		
	-60.0	0.108	5.80		
	-59.2	0.0932	5.01		
	-49.0	0.237	12.9		
	-49.0	0.227	12.3		
	-48.0	0.254	13.8		
	-40.0	0.524	28.7		
	-39.8	0.399	21.9		
	-39.0	0.486	26.7		
	-33.0	0.711	39.2		
	-33.0	0.744	41.1		
	-32.5	0.775	42.8		
n-Pr	-63.0	0.0549	3.80	31 ± 1	143 ± 4
	-60.5	0.0481	3.34		
	-60.0	0.0602	4.18		
	-52.8	0.108	7.52		
	-51.0	0.0900	6.30		
	-49.5	0.138	9.69		
	-49.5	0.125	8.76		
	-49.2	0.122	8.57		
	-48.2	0.144	10.1		
	-41.0	0.236	16.4		
	-40.8	0.258	18.2		
	-40.0	0.259	18.3		
	-38.5	0.299	21.1		
	-30.5	0.538	38.3		
	-29.5	0.527	37.6		

II

Table continued

1	2	3	4	5	6
	-25.8	0.763	54.6		
	-24.8	0.601	43.1		
	-21.8	0.958	68.9		
	-21.0	1.23	88.4		
	-18.5	1.07	77.3		
i-Pr	-48.2	0.0128	0.913	37 ± 1	140 ± 4
	-39.0	0.0204	1.47		
	-38.3	0.0244	1.76		
	-31.0	0.0538	3.91		
	-29.8	0.0498	3.63		
	-29.6	0.0477	3.47		
	-22.0	0.0900	6.60		
	-21.3	0.0865	6.35		
	-21.0	0.0793	5.82		
	-15.5	0.160	11.8		
	-15.3	0.150	11.1		
	-15.3	0.133	9.83		
	-11.5	0.201	14.9		
	-11.5	0.173	12.8		
	-11.0	0.238	17.6		
	-6.2	0.243	18.1		
	-6.0	0.250	18.6		
	-6.0	0.283	21.1		
	-1.0	0.347	26.0		
	-1.0	0.473	35.7		
	-1.0	0.331	24.8		
n-Bu	-54.2	0.0577	4.94	31 ± 2	142 ± 7
	-54.0	0.102	8.69		
	-53.0	0.108	9.24		
	-49.5	0.120	10.3		
	-49.5	0.136	11.7		
	-44.0	0.151	13.1		
	-43.0	0.193	16.6		
	-42.0	0.265	22.9		

Table continued

1	2	3	4	5	6
	-35.0	0.298	25.9		
	-34.5	0.390	33.9		
	-34.5	0.362	31.5		
	-29.2	0.450	39.4		
	-29.0	0.545	47.7		
	-25.5	0.723	63.5		
	-25.0	0.607	53.3		
	-24.8	0.854	75.0		
	-24.5	0.761	66.8		
	-24.0	0.636	55.9		
s-Bu	-41.0	0.0134	1.16	36.6±0.8	142 ± 3
	-30.0	0.0326	2.85		
	-30.0	0.0303	2.64		
	-22.5	0.0552	4.86		
	-21.5	0.0533	4.70		
	-16.6	0.0878	7.78		
	-16.0	0.0835	7.40		
	-15.2	0.0936	8.30		
	-11.0	0.129	11.5		
	-10.8	0.132	11.7		
	-5.8	0.180	16.1		
	-5.2	0.164	14.6		
	-5.0	0.171	15.3		
	-2.0	0.205	18.4		
	-2.0	0.239	21.5		
	-1.5	0.260	23.4		

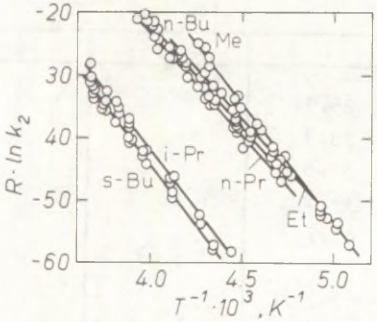

Fig. 1. Arrhenius dependencies of phosgene solvolysis in ROH alcohols.

Activation parameters of the reaction are rather low and correspond to the reaction course according to the addition-elimination mechanism[1-3]. Good correlation between the rate constants logarithms of phosgene and methyl chloroformate (MCF)[4] alcoholysis in corresponding alcohols also testifies to this (Fig. 2). The latter reaction also progresses according to the addition-elimination mechanism. The existence of linear dependence (Fig.2) as well confirms the invariability of the mechanism in the reaction series.

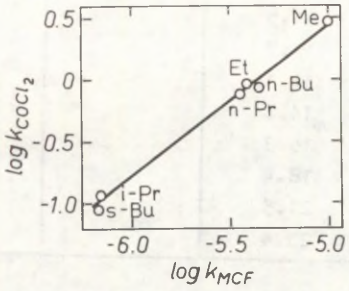

Fig. 2. Interdependence of rate constant logarithms of phosgene (25°C) and MCF (30°C) solvolysis in ROH alcohols, r = = 0.996.

We made an attempt to use the Taft equation[5] for the analysis of the effect of alcohol structure on the reaction rate. It turned out that there was no linear dependence between log k and E_s and E_s^o at -40°C. Steric constants in correspondence with the isosteric principle[7] were taken for the

RCH_2 series.

So far as alcohols in our case being reagents also act as solvents, it was of interest to evaluate their reactivity in the frames of the Kirkwood model and by the Koppel-Palm equation[6]. For tert.-butyl chloride such an approach proved to be efficient[8]. However, in case of the reaction series being now investigated, an attempt to obtain such a correlation failed. Abnormal behavior of methanol in comparison with other alcohols, made us pay attention to it. The "drop-out" of methanol from the general dependence of the alcohol structure and medium properties influence on their kinetics of phosgenation, was observed in the diluted solutions as well[2]. This fact is explained by the abnormally high associative capacity of methanol, which, as follows from works[1,2], essentially influences the kinetics process. The unusual behavior of methanol was discovered from the comparison of activation parameters and is illustrated by the Arrhenius dependences (Fig. 1). Moreover, as it can be seen from Figs. 1 and 2, alcohols may be divided into three groups: methanol, primary C_2-C_4 alcohols, secondary alcohols. Quantitatively this can be taken into account by means of the $h \cdot n_H$ supplementary term introduction into the Taft equation, where n_H is the number of α-hydrogen atoms in substituent R; h - sensitivity factor. Experimental data for -40°C processing, according to the above-mentioned equation, led to a very good correlation (2).

$$\log k_2 = (2.26 \pm 0.43) + (3.69 \pm 0.28)E_s^o - (0.88 \pm 0.13)n_H \quad (2)$$

$$N = 6, \quad R = 0.999, \quad SD = 0.04$$

The result obtained is rather difficult to interprete. The case is that the h-parameter usually characterizes the "hyperconjugation" contribution to the steric constant[6]. That is why the E_s^o scale[6] was used in Eq. (2). It is difficult to speak of the "hyperconjugation" effects on alcohol nucleophility here as alcohol does not react in the form of a monomer but in a self-associative or even "cluster" form[9]. The effect of the n_H factor on self-association is not evi-

dent. To our mind, it can be only confirmed that n_H just characterizes three different groups of alcohols, behaving differently during phosgenation.

As follows from Eq. (2), the reaction series is highly sensitive to steric hindrances. This correlates well with the addition-elimination mechanism and the earlier data on the phosgenation of alcohols in organic solvents medium[1,2].

In accordance with the results obtained, it is of interest to consider the problem of the existence of isokinetic temperature β in the reaction series. An attempt was made to find β by means of (2) as a basic eequation, and utilizing a mathematical apparatus developed in detail specially for this problem[6]. All data given in the Table were used in calculations, taking and not taking methanol into consideration. The original equation characterizing the joint effect of structural factors and temperature and comprising all possible cross terms is as follows (3):

$$R \cdot \ln k_2 = a_1 + \frac{a_2}{T} + a_3 E_s^o + a_4 n_H + a_5 \frac{E_s^o}{T} + a_6 \frac{n_H}{T} + a_7 E_s^o n_H + a_8 \frac{E_s^o n_H}{T}, \qquad (3)$$

where R is the universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$.

Regression dependence for -40°C analysis (3) with a successive elimination of insignificant terms showed that ignoring methanol, statistically significant was correlation (4).

$$R \cdot \ln k_2 = (109.7 \pm 2.2) + (3.34 \pm 0.11) \cdot 10^4 \cdot \frac{E_s^o}{T} - (1.373 \pm 0.063) \cdot 10^4 \cdot \frac{n_H}{T} - (1.19 \pm 0.16) \cdot 10^4 \cdot \frac{E_s^o n_H}{T} \qquad (4)$$

$$N = 89, \quad R = 0.992, \quad SD = 1.110$$

Equation (4) suggests that β = oo, i.e. the reaction series under study is an isoentropic one. Actually, as can be seen from the Table, for all alcohols except methanol, $\Delta S^{\neq}$ are equal in the limits of determination of accuracy. If we stillassume β to be different from the infinity, instead of

Eq. (4) the dependence should be searched in form (5):

$$R \cdot \ln k_2 = a_1 + a_2 E_s^o (1 - \frac{\beta}{T}) + a_3 n_H (1 - \frac{\beta}{T}) + a_4 E_s^o n_H (1 - \frac{\beta}{T}) \quad (5)$$

Calculation of factors a_1-a_4 and ß by means of nonlinear regression[10] yielded to:

$a_1 = 88.2 \pm 1.9$; $a_4 = 7.1 \pm 1.2$; N = 89;
$a_2 = -21.0 \pm 0.8$; ß = 1600 ± 30; R = 0.992;
$a_3 = 8.10 \pm 0.45$; SD = 1.109.

Although the positive result seems to be obtained and the ß value on the whole corresponds to the isokinetic temperature for the MCF solvolysis in aliphatic alcohols[4], Fisher's ratio test testifies to the statistical equivalence between the new equation and equation (4). However, correlation dependence (4) is preferable, for it comprises less parameters.

In case of processing the data of the Table taking methanol into consideration, as has been described above, we did not succeed in getting statistically significant correlations. Thus, as in the case of phosgenation in a solution[2], methanol acts abnormally. Phosgene methanolysis is characterized by the $\Delta H^{\neq}$ value comparable with the $\Delta H^{\neq}$ for the secondary alcohols, and a relatively high (less negative) $\Delta S^{\neq}$ value.

Experimental

Alcohols were dried and purified by conventional techniques[11], phosgene was distilled prior to solution preparation.

Kinetic measurements were carried out conductometrically[1] according to the hydrogen concentration rise. The reaction was conducted in an absolute alcohol; phosgene initial concentration comprised $(1\text{-}50) \cdot 10^{-4}$ mol/l. Conductivity meter OK-102/1 was utilized in the work. Its signal was brought out to a 056 Hitachi Recorder.

To obtain the rate constant non-shifted evaluation, the experimental data processing was conducted explicitly, minimizing the square sums discrepancies between the experimental and calculated conductivity values, according to Eq. (6):

$$\Lambda_{\infty} - \Lambda_t = (\Lambda_{\infty} - \Lambda_o)\cdot\exp(-k_1\cdot t), \qquad (6)$$

where Λ_o, Λ_t and Λ_{∞} are the conductivity values, corresponding to the initial, current and "infinite" reaction time. Value k_1 was found and Λ_{∞} and Λ_o values were ascertained during optimization. Minimization was accomplished by gradient method[10]. Errors of rate constants determination did not exceed 7 %. Calculations were carried out using an Apple II personal computer according to the original programs written in BASIC in CP/M and Apple DOS 3.3 operating systems.

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PHOTOELECTRON SPECTRA OF MOLECULES
8. KETONES*

U.H. Mölder, R.J. Pikver, and I.A. Koppel

Laboratory of Chemical Kinetics and Catalysis,
Department of Geophysics, Tartu State University,
Tartu, Estonian S.S.R.
Institute of Chemical and Biological Physics,
Academy of Sciences of the Estonian S.S.R.,
Tallinn, Estonian S.S.R.

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Photoelectron spectra (PE) of 8 ketones: FCH_2COCH_3, CF_3COCH_3, $(CF_3)_2CO$, $(F_2CH)_2CO$, $(ClCH_2)_2CO$, CF_3COCCl_3, (cyclo-$-C_3H_5)_2CO$ and $3\text{-}CF_3C_6H_4COCH_3$ have been measured. Nonempirical quantum-chemical calculation of PE spectra of these molecules using the Gaussian-80 program system (STO-3G and 3-21G basis sets) and semiempirical CNDO/2 and HAM/3 methods has been conducted. Both predicted absolute values of the ionization potentials (IP) as well as the adequacy of reflecting the relationship

$$IP = a\varepsilon_i + b,$$

where a and b are constants, between the IP_i

* The material presented has partially been used in discussing various aspects of ionization potentials' (IP) dependences on structure and proton affinities (see papers [1-5] and references therein).

measured from the PE spectra and the calculated eigenvalues of energy ($-\varepsilon_i$), show that the HAM/3 method can be favored. The IP dependences in homological series on such parameters of molecules as proton affinity (PA), binding energy (E_B) of the inner shell electrons, shifts of the OH-group stretching frequencies of phenol in case of complex formation with ketones in solution have been monitored.

Comparison of $IP_v(n_O)$ and $IP_v(\pi_{CO})$ of a wide range of carbonyl-containing compounds (aldehydes, ketones, amides, esters, carboxylic acids, halide anhydrides) with $IP(n_O)$ of ethers and alcohols, with $IP(n_N)$ of nitriles, $IP(n_S)$ of sulphur containing compounds has been carried out. $IP(\pi_{CO})$ of carbonyl containing compounds have also been compared with $IP_v(\pi_{C=C})$ of alkenes and $IP_v(\pi_{C\equiv C})$ of alkynes. It has been established that there is a correlation between the $IP(n_O)$ and $IP(\pi_{CO})$ for carbonyl-containing compounds. A new interpretation of PE spectra for a number of ketones, amides, esters and carboxylic acids has been proposed.

In the present series of papers (see[6] and the references therein), has been conducted a detailed analysis of the PE spectra of various classes of compounds. The complex approach applied[1-5] includes the empirical regularities, established between the IP molecules and other physical parameters, characterizing the electronic structure of molecules as well as the quantum-chemical calculations on different levels of theory. Special attention has been paid to establishing the electronic structure and substituent effects in the compounds with electronegative substituents.

Experimental

The applied instrumentation and the methods of determining the PE spectra were described in paper[1] of this series. The vertical ionization potentials (IP_v) have been determined as the band maximums in the PE spectra, while the adiabatic ones (IP_a) as the beginning of the band, the half-width of the argon line in the spectrum being added. The latter was also used for calibration of the spectra. The PE spectra of the ketones given in Fig. 1 are averaged representations of the results of a repeated scanning of the spectrum.

CH_3COCF_3, 3-$CF_3C_6H_4COCH_3$, CF_3COCCl_3, and $(\Delta)_2CO$ compounds were from "Aldrich", FCH_2COCH_3 and $(F_2CH)_2CO$ from "PCR" and "K&K", respectively. $(ClCH_2)_2CO$ is a commercial reagent produced in the USSR, $(CF_3)_2CO$ was obtained by dehydration (P_2O_5) of the corresponding hydrate.

The purity of the majority of reagents was tested by means of gas-liquid chromatography. In order to eliminate the dissolved gases from liquids, before registering the spectra, the substances were exposed to several freeze-thaw-freeze cycles in liquid nitrogen, followed by pumping out the remaining gaseous ingredients.

Quantum-chemical calculations of molecules were performed on a EC-1060 computer of Tartu State University Computer Center (see also[2,3]). The calculations using the semiempirical CNDO/2 method were carried out with the original parametrization, applying the "optimum" bond lengths, suggested in[7,8].

Experimental geometry was used for the semiempirical HAM/3 calculations[9]. In the absence of the data, the calculations were based on the optimum geometry found by the nonempirical methods.

The ab initio calculations with a complete optimization of the geometry were performed applying the Gaussian-80[10] program sets. In Table 1 are given the total energy values of molecules obtained in the calculations. Since the values and the order of MO energies ($-\varepsilon_i$) remarkably depend

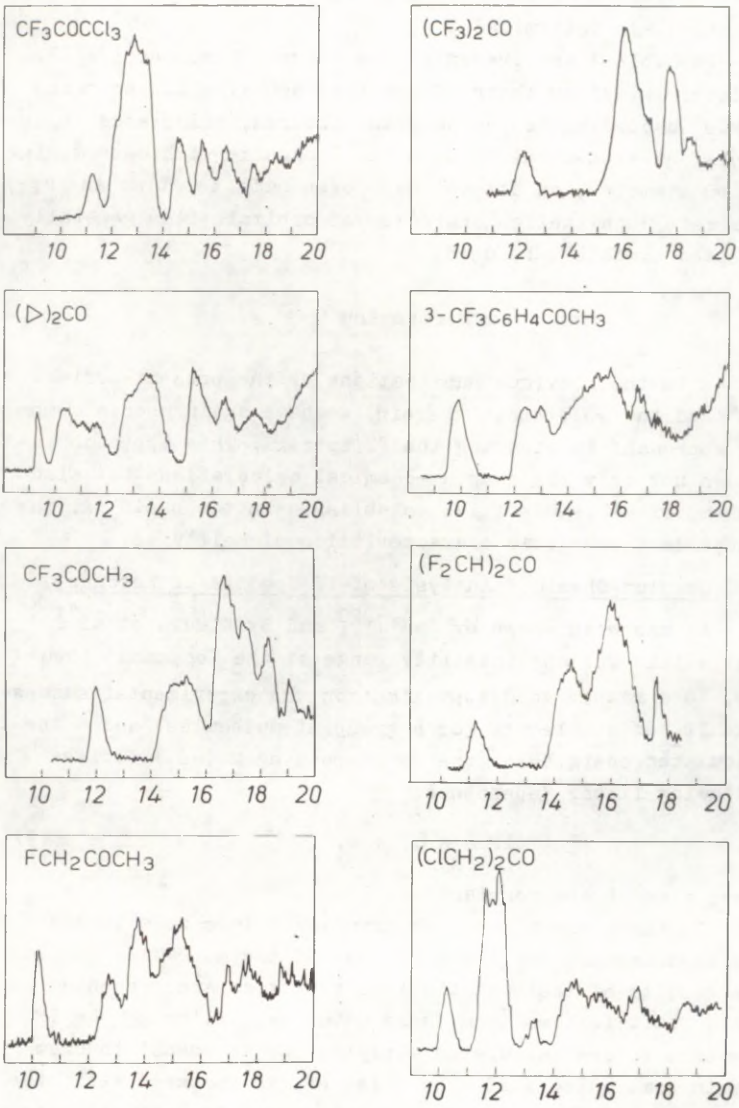

Fig. 1. PE spectra of some ketones.

on the selected conformation, in some cases the optimum conformation was determined.

In Table 1 are presented the values of successive IP, as determined from their PE spectra, and also the energies of MOs according to the Koopmans' theorem, calculated by several quantum-chemical methods. Alongside with determining the MO symmetry, an attempt has been made to find an approximate localization character of orbitals (the generally accepted symbols were used).

Discussion

As in the previous publications of the present series (see[6] and the references therein) we have again used a complex approach[5] in studying the PE spectra. This approach includes not only the quantum-chemical calculations but also the empirical regularities established on the basis of the independent energetic characteristics of molecules.

Quantum-Chemical Analysis of PE Spectra of Ketones

It has been shown by us[4,5,20] and by Kimura et al[11] that within the applicability range of the Koopmans' theorem, in a rather good approximation the experimental successive IP_i of a molecule (or a group of molecules) and the calculated energies of the corresponding MO($-\mathcal{E}_i$) fit the following linear dependence:

$$IP = a\,\mathcal{E}_i + b, \qquad (1)$$

where a and b are constants.

In the present work, observance of this relatioship has been checked for the whole set of the molecules studied. The results of their statistical treatment are presented in Table 2. It follows from these data that, although the IP absolute values calculated applying the Koopmans' theorem may in some cases differ by a few eV, if compared with the experimental ones, the given relationship is statistically quite well obeyed. In some cases such correlations enable[5,11] us to find in the PE spectra the band being dif-

Table 1

Ionization Potentials Determined from PE Spectra and Calculated by Quantum-Chemical Methods

1. $(CH_3)_2CO$

IP_v[a]	CNDO/2[b]		HAM/3[c]		STO-3G[d]		3-21G[e]	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
9.70	13.25	$9a'\ n_O$	9.93	$2b_2\ n_O$	8.76	$5b_2\ n_O$	10.93	$5b_2 n_O$
12.59	15.31	$3a''\ \pi_{CO}$	12.49	$4b_1\ \pi_{CO}$	10.81	$2b_1\ \pi_{CO}$	13.00	$2b_1 \pi_{CO}$
13.41	16.99	$8a'\ \sigma_{CO}$	13.27	$1b_2\ \sigma_{CC}, \sigma_{CH}$	13.19	$8a_1\ \sigma_{CO}$	14.57	$4b_2\ \sigma_{CH}$
14.04	18.18	$7a'\ \sigma_{CH}, n_O$	13.87	$1a_2\ \pi_{CH_3}$	13.49	$4b_2\ \sigma_{CH}$	15.14	$8a_1\ \sigma_{CO}, \sigma_{CC}$
(14.8)	19.73	$2a''\ \pi_{CH_3}$	14.12	$5a_1\ \sigma_{CO}, \sigma_{CC}$	14.31	$1a_2\ \pi_{CH_3}$	15.29	$1a_2\ \pi_{CH_3}$
15.60	22.38	$6a'\ n_O, \sigma_{CH}$	14.72	$3b_1\ \sigma_{CC}, n_O$	15.56	$7a_1\ \pi_{CH_3}$	17,10	$1b_1\ \pi_{CH_3}$
(16.1)	23.11	$5a'$	14.74	$4a_1\ n_O$	15.78	$1b_1\ \pi_{CH_3}$	17.20	$7a_1\ \sigma_{CO}$
(16.6)	24.04	$1a''$	15.52	$2b_1$	15.94	$3b_2\ \pi_{CO}, \sigma_{CC}$	17.65	$3b_2, \sigma_{CC}, n_O$

a - see[11]; b-- E_{tot} = -44.2253 a.u., this report; c - this report, experimental geometry; d - E_{tot} = -189.5360 a.u., this report, see also[12]; e - E_{tot} = -191.6774 a.u., this report, optimum geometry: CO = 1.211 Å, CC = 1.515 Å, CHI = 1.080 Å, CH = 1.085 Å, CCO = 122.47°, HCC = 109.74°, HCH = 107.92°, report[11] contains the 4-31G calculation.

Table 1 continued

2. $CH_3COCH_2CH_3$

IP_v[a]	CNDO/2[b]		HAM/3[c]		3-21G[d]		4-31G[e]	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
9.56	13.31	11a' n_O	9.69	11a' n_O	10.88	16a' n_O	9.41	16 a' π_{CH_3}
12.26	14.07	4a'' π_{CO}	12.17	4a'' π_{CO}, π_{CH_3}	12.98	4a'' π_{CO}	11.61	15a' n_O
12.66	15.59	10a' σ_{CO}, π_{CH_3}	12.33	10a' σ_{CC}	13.58	15a' π_{CH_2}	13.35	4a'' π_{CO}
13.02	16.57	9a' σ_{CC}, n_O	12.64	3a'' π_{CH_2}, π_{CO}	13.80	3a'' π_{OH_3}	14.28	3a'' π_{CH_3}
(13.5)	16.97	3a'' π_{CH_3}, π_{CH_2}	12.87	9a' π_{CH_3}	14.04	14a' π_{CH_3}	14.78	14a' σ_{CO}
14.37	18.26	8a' π_{CH_3}	14.02	8a' π_{CH_3}	15.38	13a' π_{CH_3}	15.06	13a' π_{CH_3}
14.89	21.51	2a'' π_{CH_3}	14.12	7a' n_O	15.99	2a'' π_{CH_3}	16.05	2a'' π_{CH_3}
15.34	22.00	7a' π_{CH_3}, n_O	14.85	2a'' π_{CH_3}	16.78	12a' σ_{CO}	17.44	12a' σ_{CO}
15.97	23.48	6a' π_{CH_3}	14.85	6a' σ_{CC}	17.62	1a'' π_{CH_2}	17.73	1a'' π_{CH_3}
(16.8)	25.56	5a'	15.85	1a'' π_{CH_2}	18.00	11a' σ_{CC}	18.09	11a' σ_{CC}

a - see[11,13]; b - E_{tot} = -52.9440 a.u., this report; c - this report, experimental geometry[14]; d - E_{tot} = -229.7086 a.u., this report, optimum geometry: where in $H_3Cl(CO)C2H_2C3H_3$ CO = = 1.211 Å, CH = 1.083 Å, C3CC = 110.92°, C1C = 1.517 Å, C2C = 1.544 Å, HCC = 109.93°, C1CO = = 122.52°, C2CO = 122.14° ; d - E_{tot} = -230.4544 a.u., see[11].

Table 1 continued

3. F_2CO

IP_v[a]	CNDO/2[b]			HAM/3[c]			STO-3G[d]			3-21G[e]		
	$-\varepsilon_i$	MO		$-\varepsilon_i$	MO		$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
13.6	17.28	$2b_1$	π_{CO}, n_F	13.00	$4b_2$	n_O	11.18	$5b_2$	n_O	15.02	$5b_2$	n_O
14.6	17.39	$4b_2$	n_O	14.95	$2b_1$	π_{CO}, n_F	11.23	$2b_1$	π_{CO}, n_F	15.48	$2b_1$	π_{CO}, n_F
16.6	19.89	$5a_1$	σ_{CO}, n_F	16.91	$3b_2$	$\bar{n}_O, n_F$	13.75	$8a_1$	$n_F, \bar{n}_O$	18.56	$4b_2$	n_F
							13.97	$4b_2$	n_F	18.66	$8a_1$	$\bar{n}_F, \bar{n}_O$
17.2	21.47	$3b_2$	n_F	17.32	$5a_1$	n_F						
				17.41	$1a_2$	n_F	14.48	$1a_2$	n_F	19.23	$1a_2$	n_F
19.15	22.20	$1a_2$	n_F	18.99	$4a_1$	$n_F, \bar{n}_O$	17.41	$7a_1$	$\bar{n}_O, \sigma_{CO}, n_F$	21.40	$7a_1$	$\bar{n}_O, n_F$
19.8	24.69	$4a_1$	$\bar{n}_O, n_F$	20.00	$1b_1$	n_F, σ_{CO}	17.90	$1b_1$	π_{CF_2}	21.98	$1b_1$	π_{CF_2}
21.1	26.46	$1b_1$	n_F, π_{CO}	21.17	$2b_2$	σ_{CF}	18.74	$3b_2$	σ_{CF}, n_O	22.98	$3b_2$	σ_{CF}
23.4	26.58	$2b_2$	σ_{CF}, n_O	23,57	$3a_1$	n_F	21.43	$6a_1$	σ_{CO}, n_F	25.16	$6a_1$	

a - see[15]; b - E_{tot} = -80.8557 a.u., this report;
c - this report, experimental geometry;
d - E_{tot} = -307.3079 a.u., this report, see also[12];
e - E_{tot} = -309.9044 a.u., this report, optimum geometry: CO = 1.169 Å, CF = 1.323 Å, FCO = 125.82°.

Table 1 continued

4. $(CN)_2CO$

IP_v[a]	CNDO/2[b]		HAM/3[c]		STO-3G[d]		3-21G[e]	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
12.56	14.99	n_O	11.88	$5b_2$ n_O	11.76	$2b_1$ π_{CO},π_{CN}	14.09	$2b_1$ π_{CO},π_{CN}
13.76	15.81	π_{CO}	13.24	$2b_1$ π_{CN},π_O	12.18	$7b_2$ n_O	14.37	$7b_2$ π_{CN},n_O
14.41	17.35	π_{CN},π_O			12.40	$6b_2$ π_{CN}	14.69	$1a_2$ π_{CN}
			13.53	$1a_2$ π_{CN}	12.68	$1a_2$ π_{CN}	14.90	$6b_2$ n_O
			13.55	$4b_2$ π_{CN}				
14.79	18.05	π_{CN},π_O	13.90	$6a_1$ π_{CN}	12.89	$10a_1$ π_{CN}	15.13	$10a_1$ π_{CN}
			14.20	$5a_1$ n_N				
			14.29	$3b_2$ n_N				
16.7	18.68	π_{CN}	15.86	$1b_1$ π_{CO}	14.39	$9a_1$ n_N	16.80	$9a_1$ n_N
					14.69	$5b_2$ n_N,n_O	16.97	$5b_2$ n_N
17.9	19.72	n_N	16.53	$4a_1$ $\bar{n}_O$	15.83	$1b_1$ π_{CO}	18.13	$1b_1$ π_{CO}
	19.97	n_N						

a - see[16]; b- E_{tot} = -62.3737 a.u., this report; c - this report, experimental geometry[8]; d - E_{tot} = -239.4418 a.u., this report, see also[12]; e - E_{tot} = -295.6349 a.u., this report, optimum geometry: CO = 1.202 Å,,CC = 1.444 Å, CN = 1.138 Å, CCO = 123.36°.

Table 1 continued

5. FCH_2COCH_3

IP_v^a	CNDO/2[b]		HAM/3[c]		STO-3G[d]		3-21G	
	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO	$-\varepsilon_i$	MO
10.20	13.75	11a' n_O	9.99	11a' n_O	8.80	16a' n_O	11.35	16a' n_O
12.60	14.69	4a'' π_{CO}	12.37	4a'' $\pi_{CO}, n_F, \pi_{CH_2}$	10.79	4a'' π_{CO},	13.24	4a'' π_{CO}
13.61	16.51	10a' σ_{CO}	13.27	3a'' $n_F, \pi_{CO}, \pi_{CH_2}$	12.01	3a'' n_F, π_{CO}	15.08	3a'' n_F
			13.33	10a'			15.12	15a' π_{CH_3}
14.73	17.72	3a'' n_F	14.10	9a' n_F, σ_{CH}	12.38	15a' n_F, n_O	15.96	14a' n_F
15.19	19.09	9a' n_F, σ_{CH}	14.34	8a' $\bar{n}_O$	13.66	14a' σ_{CO}, n_F	16.53	2a'' π_{CH_3}, n_F
			14.62	2a'' $\pi_{CH_2}, \pi_{CO}, n_F$			16.60	13a' $\bar{n}_O, 3\sigma_{CC}, n_F$
16.89	19.54	8a' n_F	15.93	7a' $n_F, 2\bar{n}_O$	14.23	13a' σ_{CH}, n_F	18.66	12a' n_F
							18.82	11a' $n_F, \bar{n}_O$
17.72	22.07	2a'' n_F, π_{CH_3}	17.39	1a'' n_F, π_{CH_2}	14.96	2a'' π_{CH_3}	19.45	1a'' n_F, π_{CH_2}
18.91			17.78	6a' n_F				
18.91	23.08	7a'	18.30	5a'	15.72	12a' n_F	20.97	10a' n_F

a - this report, $IP_a^{(1)}$ = 10.09 eV, $IP_a^{(2)}$ = 12.25 eV, see also[17]; b - E_{tot} = -71.2436 a.u., this report, cis-conformation; c - this report, optimum STO-3G geometry; d - E_{tot} = -286.9792 a.u., this report, trans-conformation, e - E_{tot} = -289.2000 a.u., this report, trans-conformation, optimum geometry: CO = 1.210 Å, CC = 1.510 Å, CHI = 1.080 Å, CH = 1.082 Å, CF = 1.400 Å, CCO = 125.08°, CC10 = 119.80°, HCC = 109.32°, FCC = 109.99°, HCH = 108.04°.

Table 1 continued

6. CF_3COCH_3

IP_v[a]	CNDO/2[b]			HAM/3[c]			STO-3G[d]			3-21G[e]		
	$-\varepsilon_i$	MO		$-\varepsilon_i$	MO		$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
10.94	14.28	14a'	n_O	10.87	14a'	n_O	9.16	20a'	n_O	12.53	20a'	n_O
13.74	16.21	7a''	π_{CO}	13.49	7a''	π_{CO}, π_{CH_2}	11.92	8a''	π_{CO}	14.54	8a''	π_{CO}, π_{CH_3}
14.25	17.40	13a'	σ_{CO}, π_{CH_3}	14.05	13a'	π_{CH_3}	12.75	19a'	n_F	15.86	19a'	π_{CH_3}
							12.78	7a''	n_F			
15.64	19.53	12a'	n_F	14.94	12a'	σ_{CO}	13.05	18a'	n_F, n_O	17.13	7a''	π_{CH_3}, π_{CO}
				15.03	6a''	π_{CH_2}, π_{CO}	13.31	6a''	n_F			
				15.32	11a'	n_F						
				15.42	5a''	n_F						
16.44	19.79	6a''	n_F	15.91	10a'	n_F	13.95	17a'	n_F	17.67	18a'	σ_{CO}
				16.30	4a''	n_F	14.15	5a''	n_F	17.72	6a''	n_F
17.25	20.64	11a'	n_F	16.71	3a''	n_F	14.99	16a'	n_F	17.93	17a'	n_F
				16.85	9a'	n_F				17.99	5a''	n_F
										18.12	16a'	n_F
18.04	21.18	10a'	σ_{CH}, n_F	17.32	8a'	n_O	15.40	15a'	σ_{CO}	19.26	15a'	n_F
	21.35	5a''	n_F				15.70	4a''	π_{CH_3}	19.28	4a''	n_F

a - this report, $IP_a^{(1)}$ = 10.68 eV, $IP_a^{(2)}$ = 13.18 eV, see also[17,18]; b - E_{tot} = -125.2191a.u. this report;

Table 1 continued

c - this report, experimental geometry[14]; d - E_{tot} = -481.9108 a.u., this report, oxygen of CO group is in trans-positions relative to CF bond, for cis-conformation E_{tot} = -481.9106 a.u. e - E_{tot} = -485.8629 a.u., this report, optimum geometry: CO = 1.202 Å, CCl = 1.495 Å, CC = 1.517 Å, CH1 = 1.079 Å, CH = 1.084 Å, CF1 = 1.336 Å, CF = 1.351 Å, CCO1 = 127.05°, CCO = 120.23°, HCC = 110.07 Å, HCH = 107.88°, FCC = 112.62°, FCF = 106.90°.

7. $(CF_3)_2CO$

IP_v[a]	HAM/3[b]			STO-3G[c]			3-21G[d]		
	$-\varepsilon_i$	MO		$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
12.09	11.93	$9b_2$	n_O	9.57	$12b_2$	n_O	14.05	$12b_2$	n_O
16.10	15.07	$7b_1$	π_{CO}, n_F	13.08	$7b_1$	π_{CO}	16.74	$7b_1$	π_{CO}
16.49	15.45	$5a_2$	n_F	13.11	$15a_1$	n_F	18.22	$11b_2$	n_F, n_O
	15.49	$8b_2$	n_O, n_F	13.25	$6a_2$	n_F	18.25	$15a_1$	σ_{CO}
	15.59	$6b_1$	π_{CO}, n_F	13.25	$11b_2$	n_F	18.25	$6a_2$	n_F
	15.69	$9a_1$	n_F, n_O	13.33	$14a_1$	n_F	18.43	$6b_1$	n_F
				13.33	$6b_1$	π_{CO}, n_F	18.54	$5a_2$	n_F
							18.56	$10b_2$	n_F
17.03	16.06	$7b_2$	n_F	13.79	$5a_2$	n_F	18.75	$5b_1$	n_F
	16.12	$5b_1$	n_F	13.82	$5b_1$	n_F	18.83	$14a_1$	n_F
	16.18	$8a_1$	$\bar{n}_O$						

Table 1 continued

IP_v[a]	HAM/3[b]			STO-3G[c]			3-21G[d]		
	$-\varepsilon_i$	MO		$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
17.84	16.51	$4b_1$	n_F, π_{CO}	14.17	$10b_2$	n_O, n_F	19.51	$4a_2$	n_F
	16.82	$4a_2$	n_F	14.44	$4a_2$	n_F	19.87	$13a_1$	n_F
	17.03	$3a_2$	n_F	14.58	$13a_1$	n_F	19.90	$9b_2$	n_F
	17.16	$6b_2$	n_F	14.85	$9b_2$	n_O			
	17.17	7a1	n_F						
18.49	17.69	$6a_1$	n_O	14.93	$4b_1$	n_F	20.28	$4b_1$	n_F
							20.85	$12a_1$	$\bar{n}_O$

a - this report, $IP_a^{(1)}$ = 11.67 eV, see also[15,19];
b - this report, experimental geometry[14] ;
c - E_{tot} = -774.2809 a.u., this report, see also[12] ;
d - E_{tot} = -780.8187 a.u., this report, optimum geometry: CO = 1.194 Å, CC = 1.511 Å, F1C = 1.337 Å, FC = 1.343 Å, CCO = 122.65°, FCC = 110.34°, F1CC = 109.35°

Table 1 continued

8. $(F_2CH)_2CO$

IP_v[a]	CNDO/2[b]			HAM/3[c]			STO-3G[d]		
	$-\varepsilon_i$	MO		$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
11.23	14.28	15a'	n_O	10.84	15a'	n_O	9.17	$9b_2$	n_O
14.49	17.30	14a'	σ_{CH}, σ_{CO}	13.31	14a'	n_O, n_F	12.10	$8b_2$	n_O, n_F
				13.58	13a'	n_F	12.26	$12a_1$	n_F
							12.48	$6b_1$	π_{CO}
							12.64	$11a_1$	n_F
15.91	18.32	9a"	π_{CO}	14.45	9a"	π_{CO}	12.82	$5a_2$	n_F
	18.41	13a'	σ_{CH}, n_F	14.71	8a"	n_F	12.86	$5b_1$	n_F
	19.65	12a'	n_F	14.87	7a"	n_F			
				14.97	6a"				
				15.12	12a'	n_F, n_O			
				15.15	11a'	n_F			
17.48	20.35	8a"	n_F	15.46	5a"	π_{CO}, n_F	13.68	$4a_2$	n_F
	20.67	7a"	n_F				14.04	$4b_1$	n_F
							14.08	$7b_2$	n_O, n_F
(19.0)	21.04	11a'	$\bar{n}_O, n_F$	16.76	10a'	$\bar{n}_O$	16.09	$10a_1$	σ_{CO}
19.93	21.87	6a"	n_F	17.75	9a'	π_{CF}	16.37	$3a_2$	π_{CF}

a - this report, $IP_a^{(1)}$ = 10.96 eV, $IP_a^{(2)}$ = 13.40 eV, see also[17];

Table 1 continued

b - this report, E_{tot} = -152.1492 a.u.; c - this report, optimum STO-3G geometry; d - this report, E_{tot} = -579.3391 a.u. CF- cis relative to CO- bond, optimum geometry: CO = 1.217 Å CC = 1.577 Å, HC = 1.111 Å, FC = 1.378 Å, CCO = 121.77°, HCC = 108.08°, FCC = 110.44°

9. CF_3COCCl_3

IP_v[a]	CNDO/2[b]			STO-3G[c]		
	$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
11.19	13.93	19a'	n_O, n_{Cl}	10.35	34a'	n_O
12.16	14.48	11a"	n_{Cl}	11.62	18a"	n_{Cl}
	14.51	18a'	n_{Cl}	11.66	33a'	n_{Cl}
12.51	15.20	10a"	n_{Cl}	11.72	17a"	n_{Cl}
12.81	15.87	17a'	n_{Cl}	12.46	32a'	n_{Cl}
	15.97	9a"	n_{Cl}	12.49	16a"	n_{Cl}
13.33	16.23	16a'	n_O, n_{Cl}	12.57	31a'	n_{Cl}
14.49	17.82	8a"	π_{CO}, n_{Cl}	13.56	15a"	n_F
				13.61	30a'	n_F
				13.66	14a"	π_{CO}
15.74	18.76	15a'		14.14	13a"	n_F
				14.35	29a'	n_O, n_F
16.41	20.19	14a'		14.84	28a'	n_F
	20.19	7a"		15.02	12a"	n_F
17.44	20.63	13a'		15.73	27a'	σ_{CCl}
18.31	21.63	6a"		16.21	11a"	σ_{CCl}

a - this report, $IP_a^{(1)}$ = 10.92 eV (cf.[18]), see also[17];

b - this report, E_{tot} = -171.4651 a.u.;

c - this report, E_{tot} = -1843.8710 a.u., CF and CCl cis relative to CO, optimum geometry: CO = 1.213 Å, CC1 = = 1.579 Å, CC2 = 1.600 Å, C1C1 = 1.815 Å, C1C1 = 1.819Å, C2F1 = 1.370 Å, FC2 = 1.370 Å, C1CO = 120.91°, C2CO = = 120.49°, C1C1C = 108.80°, C1C1Cl = 109.47°, F1C2C = = 107.66°, FC2F = 108.65° if $Cl1(Cl_2)C1(CO)C2(F_2)F1$.

Table 1 continued

10. $(ClCH_2)_2CO$

IP_v[a]	CNDO/2[b]			STO-3G[c]		
	$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
10.26	8.50	$8a_1$	n_{Cl}	9.77	25a'	n_O, n_{Cl}
11.54	13.54	$5b_2$	n_O	10.55	7a"	n_{Cl}
11.79	13.68	$2a_2$	n_{Cl}	10.83	24a'	n_{Cl}, n_O
11.99	15.20	$3b_1$	π_{CO}	10.98	6a"	n_{Cl}
13.54	15.20	7a'	n_{Cl}, σ_{CO}	11.51	23a'	n_{Cl}, n_O
14.64	16.41	$4b_2$	σ_{CCl}	12.40	5a"	π_{CO}
15.51	17.43	$2b_1$	n_{Cl}	13.25	22a'	σ_{CCl}
16.82	17.73	$6a_1$	σ_{CO}, n_{Cl}	13.62	21a'	n_{Cl}
18.78	20.69	$1a_2$	π_{CH_2}	15.84	20a'	σ_{CO}

a - this report, $IP_a^{(1)}$ = 10.15 eV (cf.[18]), $IP_a^{(2)}$ = = 11.33 eV;

b - this report, E_{tot} = -75.1100 a.u.;

c - this report, E_{tot} = -1097.5222 a.u., optimum geometry: CO = 1.215 Å, CC = 1.555 Å, HC = 1.091 Å, CCl1 =1.805Å, CCl2 = 1.810 Å, CCO = 121.43°, HCC = 110.29°, Cl1CC = = 110.96°, Cl2CC = 114.03° if $Cl1CH_2(CO)CH_2Cl2$, Cl1 is cis and Cl2 trans relative to CO bond.

11. cy-Pr_2CO

IP_v[a]	STO-3G[b]			HAM/3[c]		
	$-\varepsilon_i$	MO		$-\varepsilon_i$	MO	
9.27	8.56	$9b_2$	n_O [d]	9.41	$6b_2$	n_O [d]
10.35	9.35	$5b_1$	π_{CO} [d]	10.59	$6b_1$	π_{CO} [d]
11.01	10.58	$8b_2$	n_O, σ_{CC}	10.66	$5b_2$	n_O, σ_{CC}
				10.71	$2a_2$	σ_{CC}
11.49	10.77	$4a_2$	σ_{CC}, π_{CH_2}	10.82	$8a_1$	σ_{CC}
12.80	11.13	$12a_1$	σ_{CC}	12.58	$5b_1$	π_{CH_2}
				12.66	$4b_1$	π_{CH_2}

Table 1 continued

IP_v[a]	STO-3G[b] $-\varepsilon_i$	MO		HAM/3[c] $-\varepsilon_i$	MO	
13.50	12.84	$11a_1$	σ_{CO}	13.20	$4b_2$	
	13.35	$4b_1$	π_{CH_2}	13.26	$3b_1$	π_{CO}[d]
	13.46	$3a_2$	π_{CH_2}	13.29	$7a_1$	σ_{CO}
	13.58	$3b_1$	π_{CO}[d]			
15.21	13.80	$7b_2$		14.81	$3b_2$	
	15.41	$10a_1$	$\bar{n}_O$	14.95	$6a_1$	$\bar{n}_O$
16.49	16.14	$6b_2$		15.60	$5a_1$	
				15.86	$2b_2$	
17.62	17.02	$9a_1$		16.75	$4a_1$	

a - this report, $IP_a^{(1)}$ = 9.31 eV;

b - this report, E_{tot} = -341.4237 a.u., see also[12], optimum geometry: CO = 1.22 Å, C-C(C_3H_5) = 1.53 Å, CCO = 121.1°, CH = 1.08 Å, CC(in C_3H_5) = 1.51 Å

c - this report, STO-3G geometry

d - for the IP(π_{CO}) the arithmetic mean (≈11.9 eV) from the 2nd and 6th PES band was used.

12. 3-$CF_3C_6H_4COMe$

IP_v[a]	HAM/3 $-\varepsilon_i$			
9.86	9.41,	9.96	10.12	
12.47	11.90	12.58	11.61	12.75
13.02	13.07			
15.04				
15.57	15.54	15.62	15.74	
16.67	16.98			

a - this report, $IP_a^{(1)}$ = 9.61 eV, $IP_a^{(2)}$ = 12.03 eV.

ficult to measure because of the band overlapping.

Table 2 shows that transition from the semiempirical calculation by the CNDO/2 method to the nonempirical calculations (even in the case of the minimal basis set) tends generally to give a spectrum of eigenvalues being in a better correlation with the experimental PES (the slope is closer to unity, the intercept and the errors of these parameters are decreasing but the mean-square deviation remains unsatisfactory). Basis set extension in the case of nonempirical calculations of the PES in the framework of the Koopmans' theorem with a transition to the split valence 3-21G basis set is accompanied by a certain increase of the accuracy of the description of the PE spectra. As to the nonempirical calculations, progress can be made exceeding the limits of the Hartree-Fock technique, using either the traditional CI method as it has been done by Kimura et al.[11] or some other methods.

Table 2 again confirms an evident prevalence of the HAM/3 technique, specially parametrized for calculating the PE spectra not only over the simple semiempirical CNDO/2 method but also over any other nonempirical HF calculations at minimal or split-valence basis set (STO-3G, 3-21G) level applied in the present research. Under other similar conditions, the adequacy of the PE spectra calculation results of small molecules and even anions according to the HAM/3 technique successfully compete[9,21] with those obtained in calculations using the post-Hartree-Fock approaches.

The results of nonempirical calculations given in Table 2 (see also the correlation diagram of the MO energies calculated in the 3-21G basis set in Fig. 2) confirm that in the case of ketones, holds the empirically established perfluoralkyl effect[15] (if the CF_3 group is substituted for the methyl group, all MO of the stable region of the molecule, i.e. the ionization center, should undergo a practically parallel shift without any changes in their succession or symmetry).

It can be mentioned that the results of the analysis of the PE spectra of the compounds studied in the present

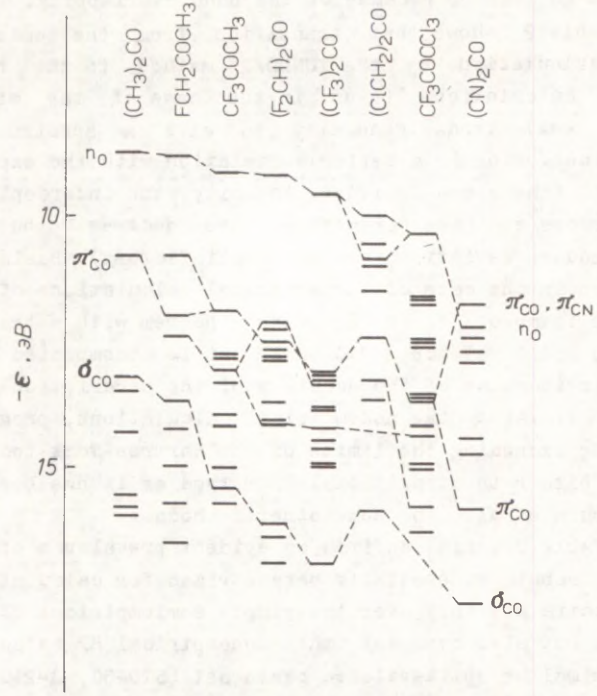

Fig. 2. Correlation diagram (3-21G basis set) of eigenvalues of energy of carbonyl-containg X_1X_2CO compounds.

work in terms of various quantum-chemical methods are in a satisfactory correlation (with the exception of a few details only). In the case of all compounds used, almost all calculation methods (see Table 1) refer to a rather substantial mixing of orbitals, both with those having either similar or different symmetries. Thus, a very significant mixing of or-

Table 2

Results of Regression Analysis of Calculated PE Spectra - Eigenvalues ($-\varepsilon_i$) According to Eq. (1)[R]

Molecule	Calc. method	a	b	r	s	n
1	2	3	4	5	6	7	8
1	$(CH_3)_2CO$	CNDO/2	0.586(0.066)	2.79(1.30)	0.970	0.62	8
		STO-3G	0.860(0.065)	2.51(0.88)	0.983	0.44	8
		3-21G	0.962(0.075)	-0.43(1.11)	0.985	0.42	8
		4-31G	0.981(0.069)	-0.79(1.06)	0.985	0.41	8
		HAM/3	1.269(0.069)	-3.14(0.95)	0.991	0.32	8
2	F_2CO	CNDO/2	0.812(0.058)	0.16(1.31)	0.985	0.62	8
		3-21G	0.921(0.054)	-0.22(1.12)	0.991	0.42	8
		HAM/3	0.965(0.034)	0.56(0.63)	0.996	0.31	8
		STO-3G	0.892(0.040)	4.10(0.64)	0.994	0.39	8
3	$(CF_3)_2CO$	CNDO/2	0.810(0.085)	0.42(1.77)	0.978	0.69	9
		STO-3G	1.250(0.027)	-0.16(0.42)	0.998	0.26	9
		HAM/3	1.102(0.024)	-0.89(0.44)	0.998	0.26	9
		3-21G	0.976(0.078)	-1.24(1.47)	0.984	0.53	7
4	FCH_2COCH_3	CNDO/2	0.828(0.077)	-0.16(1.42)	0.979	0.68	8
		STO-3G	1.202(0.069)	-0.48(0.89)	0.990	0.42	8
		3-21G	0.858(0.033)	0.84(0.55)	0.995	0.29	8
		HAM/3	1.202(0.069)	-0.48(0.89)	0.990	0.42	8
5	CF_3COCH_3	CNDO/2	0.936(0.077)	-2.10(1.44)	0.987	0.47	7
		STO-3G	1.122(0.062)	0.50(0.82)	0.992	0.33	7
		3-21G	1.028(0.069)	-1.76(1.14)	0.989	0.40	7
		HAM/3	1.084(0.020)	-0.90(0.30)	0.999	0.11	7
6	CF_3COCCl_3	CNDO/2	0.877(0.033)	-0.88(0.59)	0.995	0.27	10
		STO-3G	1.253(0.054)	-2.30(0.73)	0.992	0.32	10
7	$(F_2CH)_2CO$	CNDO/2	1.121(0.062)	-4.87(1.18)	0.994	0.40	6
		STO-3G	1.159(0.066)	0.72(0.90)	0.997	0.39	6
		HAM/3	1.276(0.032)	-2.57(0.48)	0.999	0.17	6

Table 2 continued

1	2	3	4	5	6	7	8
8	$(ClCH_2)_2CO$	CNDO/2	0.670(0.091)	3.11(1.46)	0.941	1.01	9
		STO-3G	1.458(0.082)	-3.75(1.00)	0.989	0.44	9
9	$CH_3COC_2H_5$	CNDO/2	0.476(0.059)	4.92(1.11)	0.943	0.74	10
		3-21G	0.838(0.040)	1.44(0.63)	0.993	0.21	10
		4-31G	0.698(0.077)	3.54(1.19)	0.965	0.47	10
		HAM/3	1.243(0.049)	-2.67(0.68)	0.995	0.18	10
10	$(CN)_2CO$	CNDO/2	1.037(0.150)	-3.09(2.63)	0.960	0.61	6
		STO-3G	1.151(0.061)	-0.20(0.83)	0.996	0.18	6
		3-21G	1.233(0.111)	-4.24(1.75)	0.984	0.39	6
		HAM/3	1.177(0.076)	-1.75(1.12)	0.994	0.22	6
11	$(\Delta)_2CO$	STO-3G	0.850(0.022)	2.25(0.22)	0.992	0.12	8
		HAM/3	1.127(0.027)	-1.36(0.36)	0.998	0.19	9

* a and b are the regression coefficients of Eq. (1), in parentheses are given their statistical deviations; r is the correlation coefficient; s denotes standard deviation (in eV); n - the number of points in a sample.

bitals can be observed in the case of F_2CO (Table 1, No 3) when the π_{CO} orbital gets mixed with the n_F orbital, leading to the destabilization of π_{CO} MO and to the shifts of its energy towards HOMO ($4b_2$ according to HAM/3, $5b_2$ for STO-3G and 3-21G basis sets) with the n_O character[*].

As to this compound, the orbitals with the n_F and σ_{CO}, $\bar{n}_O$ and n_F characters also get mixed (at the STO-3G level, the triple mixing of $\bar{n}_O$, σ_{CO} and n_F orbitals can also take place).

[*] It is possible that taking into consideration the aforesaid, for IP(π_{CO}) of this compound should be used the arithmetic mean from the $2b_1$ and $1b_1$ orbitals (i.e., (14.6+21.1)/2=17.9 eV) instead of the second IP from the experimental spectrum.

A certain, though remarkably less substantial mixing of the n_F and π_{CO} orbitals can be predicted also for FCH_2COMe, $(CF_3)_2CO$, $(F_2CH)_2CO$, (HAM/3) but not for CF_3COCH_3 and CF_3COCl_3 (see Table 1). For the latter compound, the CNDO/2 method (contrary to the STO-3G calculations) foretells the mixing of the π_{CO} and n_{Cl} orbitals. Mixing of two orbitals of the π-symmetry can also be predicted for acetone, MeCOEt, $(CN)_2CO$, CF_3COMe, two σ or/and n-orbitals for acetone, MeCOEt (only in the case of the CNDO/2 method), F_2CO, FCH_2COMe, CF_3COMe (CNDO/2), $(CF_3)_2CO$, $(F_2CH)_2CO$, CF_3COCCl_3 and $(ClCH_2)_2CO$. The n_F- π_{CH_2} mixing can take place in case of FCH_2COMe (HAM/3 and 3-21G). As to the latter compound (cf. F_2CO), a triple mixing of orbitals (method HAM/3 and the 3-21 basis set) can be observed (see Table 1, No 5).

It could be stated on the basis of the results of calculations (see Table 1) that there cannot actually be any serious disagreement about the n_O nature of HOMO (exceptions are the 4-31G calculations of MeCOEt, CNDO/2 calculations of F_2CO, CF_3COCCl_3 and $(ClCH_2)_2CO$, STO-3G and 3-21G calculations of $(CN)_2CO$).

However, the situation is much more complicated if the identification of the π_{CO} orbitals is concerned (especially with such compounds, in the case of which the quantum-chemical calculation methods foretell its mixing with the orbitals of some other types).

Nevertheless, a comparative analysis of the results of several calculation methods at different theoretical levels refers to some general regularities of the MO localization. On the other hand, the results of the quantum-chemical interpretation of the PE spectra can be confirmed by the results of their analysis applying the methods of comparison and correlation equations in the framework of empirical relationships.

Analysis of PE spectra of Carbonyl-Containing Compounds in Empirical Dependences between Structure and Ionization Potentials

As it has been established in[3], there exists a linear dependence in the homological series

$$PA(B) = \alpha + \beta\, IP(B), \qquad (2)$$

where α and β are constants, between the proton affinity PA(B) of base B and its ionization potential IP(B), corresponding to the elimination of the electron from the protonation center. It means that only the IP(B) values, corresponding to the orbitals which are more exactly localized at the protonation center, should obey Eq. (2). The regression analysis of the experimental data for aldehydes and ketones in the coordinates of Eq. (2) yielded the following results:

$$PA(B) = 341.9(6.7) - 0.649(0.029)IP_a(B),\ r = 0.979,$$
$$s = 2.5\ \text{kcal/mol},\ n = 23 \qquad (3)$$

and $PA(B) = 327.7(6.6) - 0.581(0.029)IP_v(B)$,
$r = 0.976$, $s = 2.7$ kcal/mol, $n = 22$.

In the parenthesis are given the statistical deviations of the corresponding regression coefficients, r - the correlation coefficient; s - standard deviation; n - number of points in a sample (for the PA values see[5,22]).

Analysis of the interrelations[3,5] between the valence shell IP and the binding energy of inner shell electrons of the $E_B(1s0)$ atom of oxygen being the ionization center, found according to the ESCA method, give in the case of aldehydes, ketones and some other carbonyl compounds the following equation:

$$IP(n_0) = 0.968(0.036)E_B(1s0) - 511.11(14.90)$$
$$n = 0.997;\ s = 0.22\text{eV};\ n = 38 \qquad (4)$$

It should be mentioned that halide anhydrides and formaldehyde do not satisfy relationship (4), they sharply devi-

ate toward greater IP. The physical reason of these deviations is not quite clear yet (see also below). One should pay attention to the fact that the slope of the straight line corresponding to relationship (4) practically coincides with unity. Hence the important conclusion about the approximately equal susceptibility to structural effects of the ionization potentials of valence and inner or intermediate shells emerges (we have referred to it in reports[3,5]).

In literature, a comparatively little attention has been paid to comparison of the IP values and to the shifts of the OH-stretching frequencies of phenol in the case of complex formation in the CCl_4 solution ($(\Delta\nu)_{PhOH}$), the so called B-parameter[5] of liquid phase basicity of solvents). It has been shown[1,5,24] that for some classes of compounds, these shifts, as a rule, tend to increase symbatically with the increase of the gas-phase basicity or proportionally to the decrease of ionization potentials of the corresponding compounds. It can actually be proved that for alkyl-substituted aliphatic ketones the $IP(n_O)$ is increasing proportionally to the drop of their general basicity ($\Delta\nu_{PhOH}$) according to equation

$$IP(n_O) = 1.74(0.99) - 0.036(0.04)\Delta\nu_{PhOH} \quad (5)$$
$$r = 0.959,\ s = 0.10\ eV,\ n = 6$$

We have also found[5] that in the case of the mentioned compound series, the increase of absolute (gas-phase) basisity of ketones is accompanied by the decrease of their $\Delta\nu_{PhOH}$ parameters.

The reason of this rather interesting anomaly is not clear yet. Quite possible that it can be explained by different dependences of the PA, PI values on the one hand, and on the other hand, of the B values on the polarizability factor[2,25], which has an important role when determining the gas phase basicity and the ionization potentials of the alkyl-substituted ketones. But in the liquid phase, its role may turn out to be rather insignificant, sometimes even negligible.[23] It should be mentioned that in the case of car-

bonylic compounds, containing an electron-donor group in the α-position toward the CO group (amides, esters, carboxylic acids), such anomalous interrelations between the PA or IP and B are not observed. The analysis conducted by us showed that such "anomalies" can crop up also when the PA or B values are compared with the ^{17}O chemical shifts (see[26] for experimental data), for instance, in the alkyl-substituted alcohols and ethers. In the latter cases, the displacement of chemical shifts of oxygen toward a weaker field is accompanied by an increase of the corresponding PA values or by a decrease of the corresponding IP.

As to the interpretation of the PE spectra, the method of comparison of IP proved rather fruitful in a series of similar compounds[5,24]. Really, proceeding from the assumption about the invariant mechanism in the compound series $X - Y_i$ and $X - Y_j$, if the nature of substituent X is varied at the fixed ionization centers Y_i and Y_j, existence of linear dependences of the following type can be expected:

$$IP(X - Y_i) = \alpha' + \beta' IP(X - Y_j), \qquad (6)$$

where α' and β' are constants.

The observance of Eq.(6) evidently refers to the similarity level of the ionization centers Y_i and Y_j. If the substituent effects lead to a change of the nature of the ionization center, the ionization mechanism will also undergo a change, such a situation cannot satisfy the conditions of Eq. (6). Formally, a correlation of this type should hold if the IP of two comparable series of compounds depend on general internal factors[5,24].

Table 3 comprises the results of statistical data treatment (see also Figs. 3-11) in terms of Eq. (6). The $IP(n_O)$ and /or $IP(\pi_{CO})$ of various carbonyl-containing compounds (alhehydes, ketones, amides, esters, carboxylic acids, halide anhydrides) have been compared with the corresponding IP of ethers and alcohols ($IP(n_O)$), alkenes ($IP(\pi_{C=C})$), alkynes ($IP(\pi_{C\equiv C})$), nitriles ($IP(n_N)$, $IP(\pi_{C\equiv N})$), sulphides ($IP(n_S)$).

In the case of statistical test of Eq. (6), both experimental data and their interpretations from the original lit-

Table 3

Statistical Treatment of Data According to Eq. (6) from[a]

Compound series compared, types of compared orbitals	α'	β'	r	s	n
1 2	3	4	5	6	7
1. XCHO, XCN					
a) n_O, n_N	-2.18 (0.82)	0.947 (0.061)	0.984	0.11	10
b) $\pi_{C=O}$, $\pi_{C\equiv N}$	2.41 (1.00)	0.888 (0.076)	0.968	0.20	11
2. XCOMe, XCN					
a) n_O, n_N	-0.67 (1.08)	0.794 (0.080)	0.971	0.13	8
b) $\pi_{C=O}$, $\pi_{C\equiv N}$	6.11 (1.29)	0.530 (0.100)	0.908	0.23	8
3. XCHO, XCOMe					
a) n_O, n_O	-0.80 (0.47)	1.129 (0.046)	0.987	0.13	17
b) $\pi_{C=O}$, $\pi_{C=O}$	-4.02 (0.95)	1.378 (0.075)	0.984	0.23	13
4. X_1OX_2, X_1X_2CO and X_1SX_2, X_1X_2CS n_O, n_S	-3.36 (0.35)	1.525 (0.039)	0.990	0.13	32
5. X_1X_2CO, X_1OX_2 n_O, n_O	4.32 (0.39)	0.526 (0.037)	0.974	0.13	13
6. X_1X_2CO, X_1SX_2 n_O, n_S	2.44 (0.53)	0.823 (0.055)	0.982	0.19	10
7. X_1X_2CO, $X_1X_2C=CH_2$ $\pi_{C=O}$, $\pi_{C=C}$	-7.24 (1.19)	2.061 (0.117)	0.985	0.28	11
8. X_1X_2CO, $X_1C\equiv CX_2$ $\pi_{C=O}$, $\pi_{C\equiv C}$	1.92 (0.46)	1.101 (0.041)	0.994	0.12	10
9. X_1X_2CO, X_1X_2CS $\pi_{C=O}$, $\pi_{C=S}$	6.84 (1.54)	0.524 (0.122)	0.851	0.45	9

Table 3 continued

;1	2	3	4	5	6	7
10.	X_1X_2CO (aldehydes, ketones, amides), see text for $\pi_{C=O}$, n_O comparison	0.21 (0.86)	1.296 (0.080)	0.967	0.30	20
11.	X_1COOX_2, XCOOH, comparison of $\pi_{C=O}$, n_O	-3.67 (1.81)	1.384 (0.168)	0.916	0.30	15

[a] For marking, see the text (α', β') and Table 2 (r,s,n).

erary sources or reviews (see[5,11,27-31] for a review and further references) and our own results from the present series of reports* or from other sources were used.

A number of relationships given in Table 3 are presented in Figs. 3-11.

The relationships presented in Table 3 are of special interest from the point of view of interpretation of the PE spectra of carbonyl-containing compounds, containing an electron-donor group attached to the C=O group (halide atom for halide anhydrides, NX_1X_2 and OX_1 groups, respectively, for amides and esters (or carboxylic acids), which often, alongside with the carbonyl group can turn into a competing ionization center. It is evident that the existence of similar ionization centers significantly complicates the interpretation of the spectrum, favoring a substantial mixing of orbitals.

* A more detailed presentation of our experimental data on the PE spectra of amides, esters and carbonic acids as well as those given in literature can be found in[22]. The results obtained have been taken into consideration when checking Eq. (6) of this work.

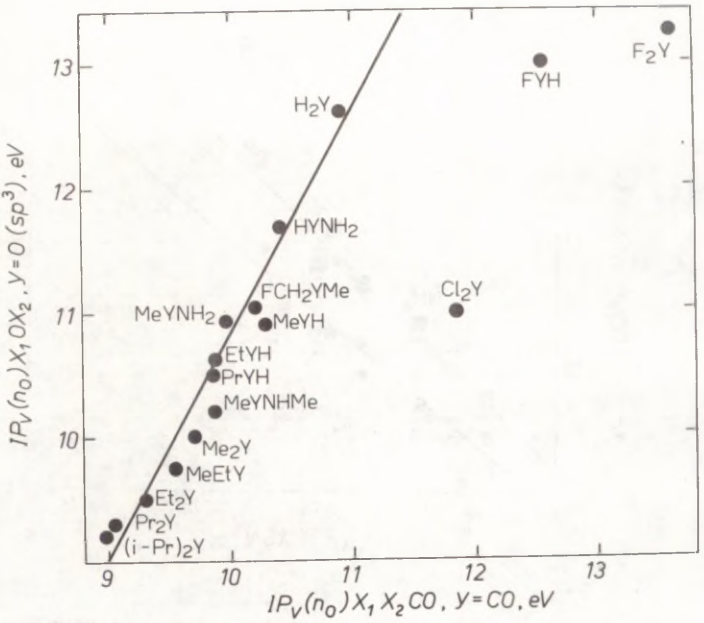

Fig. 3. Comparison of $IP_v(n_O)$ of X_1OX_2 and X_1COX_2 compounds.

In order to check determining the n_O orbitals for the above-mentioned carbonyl-containing compounds, the $IP_v(n_O)$ of these compounds were compared with the $IP_v(n_O)$ of alcohols and ethers (Fig.3), with the $IP_v(n_N)$ of nitriles (Fig. 4), of $IP_v(n_S)$ sulphides (Table 3, No 6).

In the case of these comparisons, the plots corresponding to the $IP_v(n_O)$ of the compounds, in which a halogen (FCHO, F_2CO, Cl_2CO, ClCOMe, FCOMe) is attached directly to the carbonyl group, do not obey the linearities given in

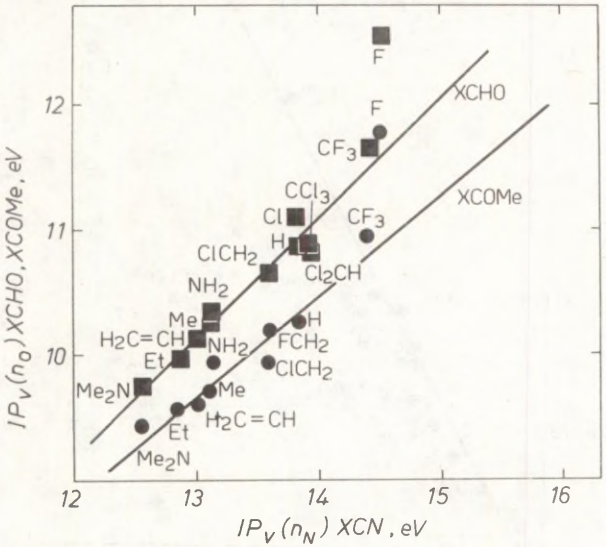

Fig. 4. Comparison of $IP_v(n_O)$ of MeCOX and XCHO compounds and $IP_v(n_N)$ of nitriles XCN.

Table 3.

The deviations from the linearity are especially great in Fig. 3. where the deviations from the plots of $IP(n_O)$ in the case of the F_2O, FOH and Cl_2O compounds towards the highly underestimated $IP(n_O)$ values are 4.0, 2.7 and 3.3 eV, respectively.[*] For instance, in the case of comparison of the $IP(n_O)$ of F_2O with $IP(n_O)$ of F_2CO, the $IP(n_O)$ = 17.6 eV would satisfy the conditions of Eq. (5) from Table 3 (assuming that $IP(n_O)$ for F_2CO is 13.6 eV). The latter value is rather close to the expected one[33] (16.7 eV), for the so

[*] The deviations are a bit smaller when the $IP(n_S)$ of sulphides and the $IP(n_O)$ of carbonyl-containing compounds are compared (Table 3, No 6).

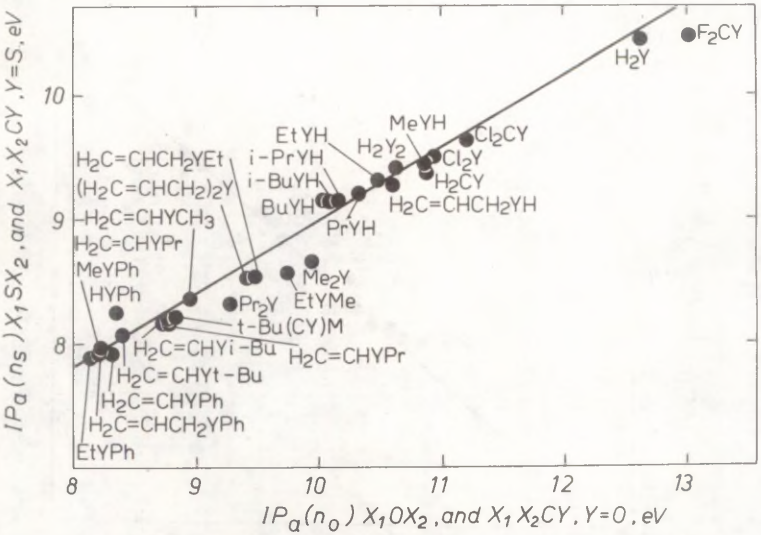

Fig. 5. Comparison of $IP_v(n_O)$ of X_1OX_2 and X_1X_2CO compounds with $IP_v(n_S)$ for X_1SX_2 and X_1X_2CS compounds.

called ionization potential of the localized (2p) orbital (LOIP). The corresponding $IP(n_O)$ values for FOH and Cl_2O which satisfy series 5 from Table 3 would be 15.7 and 14.3 eV, respectively.

Regardless of the physical nature of such deviations of $IP(n_O)$ of halide anhydrides from the straight line in the coordinates of Eq (6), they show that the effect of the halide atom directly attached to the CO-group on one hand and to the sp^3 oxygen or to sulphur and CN-group, on the other hand, is different.

At the same time, in case of comparison of the $IP(n_O)$ values for two compound series (MeCOX and HCOX and comparing the compounds of general formulae X_1OX_2 and X_1X_2CO with sulphur-containing compounds of the $X_1S_2X_2$ and X_1X_2CS types (see Fig. 5)), such deviations of individual plots were not observed for halide anhydrides.

The straight lines in Figs. 7 and 8 enable us to

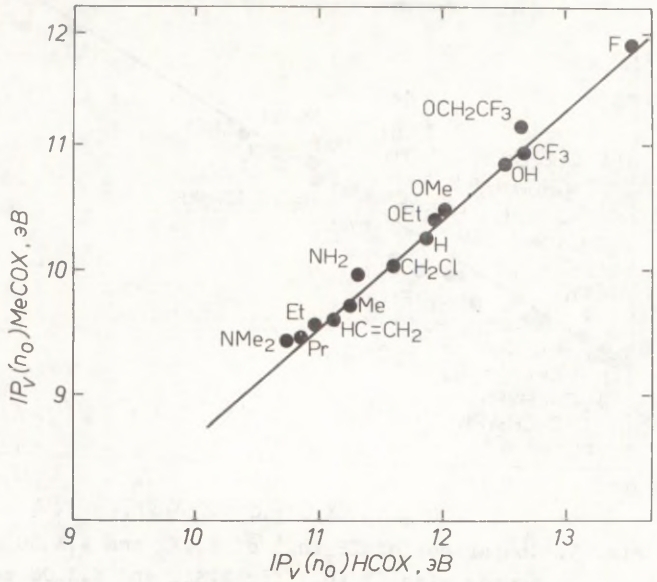

Fig. 6. Comparison of $IP_v(n_O)$ in two series of carbonyl-containing compounds, MeCOX and HCOX.

check the correctness of assignment of the π_{CO} orbitals of carbonyl-containing compounds, comparing IP(π_{CO}) with IP($\pi_{C=C}$) for substituted alkenes, or with IP($\pi_{C\equiv C}$) for the alkyne derivatives.

It can be seen that in both cases, statistically satisfactory linear relationships between the mentioned values have been followed, which evidences about closeness of the compared characteristics and refers to a correct interpretation of the band in the PE spectra. According to Table 3 analogous linearities have also been observed between IP($\pi_{C=O}$) and IP($\pi_{C\equiv N}$) (Fig. 9), IP($\pi_{C=O}$) (HCOX) and IP($\pi_{C=O}$) (MeCOX) (Fig. 6), IP($\pi_{C=O}$) and IP($\pi_{C=S}$) (series 9). It is worth mentioning that in certain cases, comparisons of ionization potentials corresponding to the electron removal from the orbitals of different symmetry

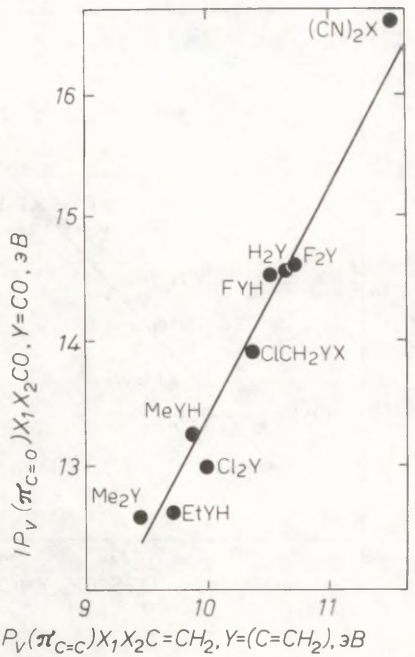

Fig. 7. Comparison of IP(π_{CO}) values of carbonyl-containing X_1X_2CO compounds with IP($\pi_{C=C}$) values for substituted alkenes.

(n_O and $\pi_{C=O}$ in the case of carbonyl-containing compounds, n_N and $\pi_{C\equiv N}$ for nitriles) in the same molecule, a certain parallelism between these values has also been observed. It can also be seen from Fig. 11, drawn up using the interpretation of the PE spectra of carbonyl-containing compounds from the above-mentioned sources as well as from this series of publications that the points for aldehydes, ketones and a number of amides (for the latter compound group, the interpretation of the PE spectra from[29,30,32] has been used) are situated on the same (upper) straight line.

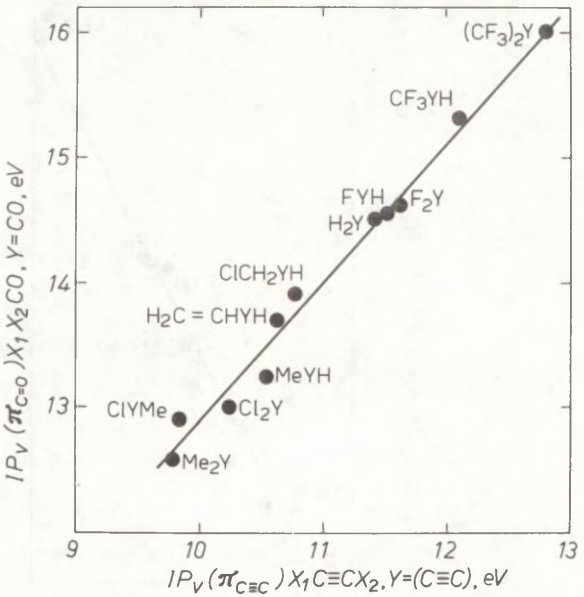

Fig. 8. Comparison of $IP_v(\pi_{CO})$ values of carbonyl-containing X_1COX_2 compounds and $IP_v(\pi_{C\equiv C})$ of substituted alkynes.

The points for carboxylic acids, esters and amides (in case of the latter, the interpretation of the spectrum, suggested in original reports[34,35] and in[27,28] was applied) lie on another straight line parallel to the former one, which is shifted by ≈3 eV lower on the ordinate axis, while F_2CO and HCOF (the second IP were used as $IP(\pi_{CO})$) will not lie on neither of these two straight lines. The slopes of the latter show that the C=O bond orbitals of the π-symmetry are 1.3-1.4 times more susceptible to the effect of molecular structure than the corresponding n_O orbitals of oxygen lone pairs of the C=O group.

Owing to the existence of two interacting and competitive ionization centers in the molecule, as well as because

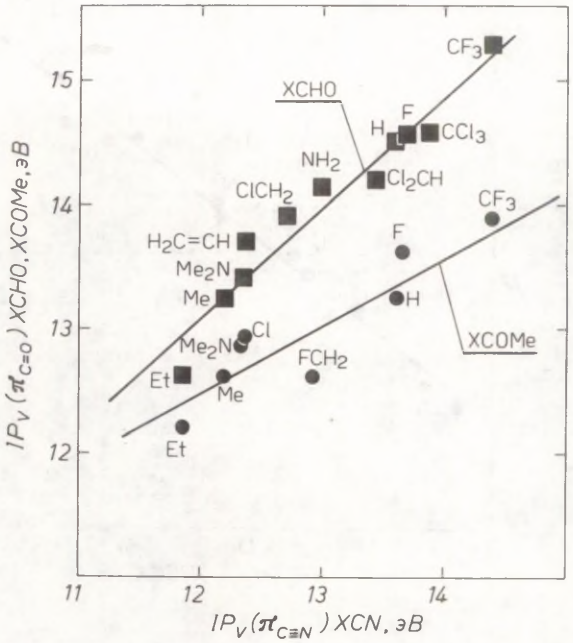

Fig. 9. Comparison of $IP_v(\pi_{CO})$ values of MeCOX and XCHO compounds and $IP_v(\pi_{C\equiv N})$ of nitriles XCN.

of remarkable difficulties in determining the correct conformation of a molecule, the analysis of the PE spectra of amides (the same concerns also the analysis of the PE spectra of carboxylic acids, esters and anhydrides of carboxylic acids) is far more complicated a problem than the analysis of the PE spectra of aldehydes and ketones. Therefore, the assignment of the MOs suggested in various reports[27-30,32,34,35] differs even in the case of determining the nature and succession of the first two or three orbitals.

In Fig. 11, when comparing the $IP(n_O)$ and $IP(\pi_{CO})$, in the case of $HCONH_2$, $MeCONH_2$, CF_3CONH_2, FCH_2CONH_2, $HCONMe_2$, $HC{\equiv}CCONH_2$, $H_2C{=}CHCONH_2$, the third ionization potentials

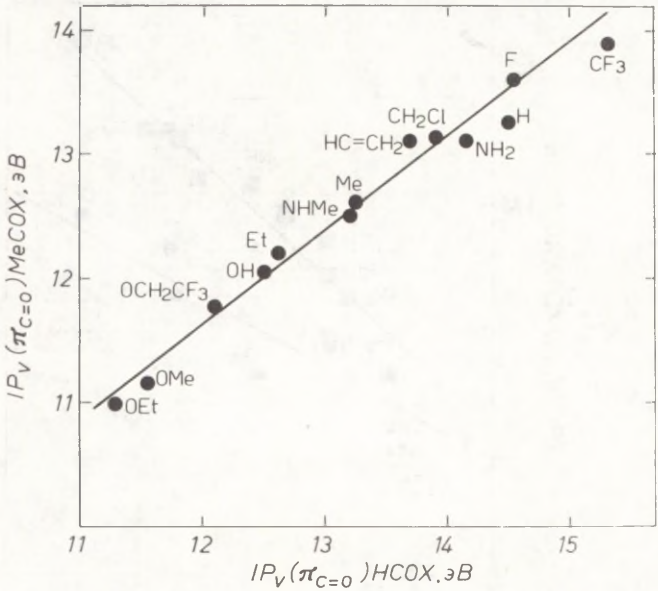

Fig. 10. Comparison of $IP_v(\pi_{C=O})$ in two series of carbonyl-containing compounds.

from the PE spectra were used (mainly employing the interpretations of[30,32]) as $IP(\pi_{C=O})$.

If for the amides of this group (HCONHMe, MeCONHMe, $(H_2N)_2CO$, $MeCONMe_2$) the third IP from the PE spectra of these compounds[32] is used as $IP(\pi_{C=O})$, these amides will also be situated on the upper straight line. The validity of such an interpretation of the PE spectra of these compounds is confirmed by the fact that it is self-consistent also with the results of the rest of correlations for these amides according to Eq. (6) (see Table 3 and Figs. 3,4,5,6,9, 10,11).

It should be mentioned that using for tetramethyl urea the approach suggested by us[32] on the basis of nonempirical

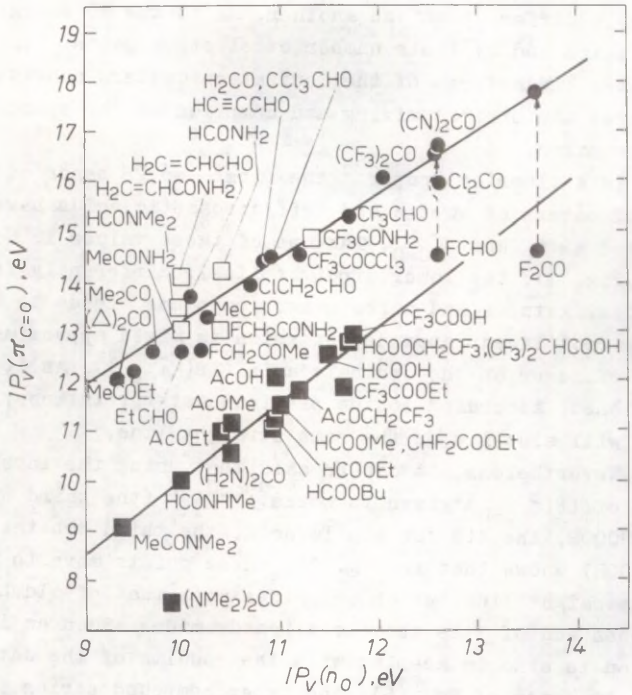

Fig. 11. Comparison of vertical ionization potentials $IP(\pi_{C=O})$ and $IP(n_O)$ in terms of Eq.(6). For explanations, see text.

calculations (STO-3G basis set) (the 4th band in the PE spectrum corresponds to $IP(\pi_{C=O})$), this compound would also lie on the (upper) common straight line in the coordinates of Eq. (6) in Fig. 11, like aldehydes and ketones.

The analysis of the PE spectra of carboxylic acids and their esters is most likely to be a far more serious problem in comparison with the analysis of the PE spectra of amides, since in the case of amides, unlike the present compound group, the competitive ionization centers usually re-

markably differ from one another, as to the MO energies of lone pairs and by their number of electron pairs. Closeness of these parameters of the ionization centers considerably promotes the orbital mixing and complicates the spectrum interpretation.

In a classical paper[35] the first two PE bands of a number of esters of acetic and trifluoroacetic acids have been treated as n_O and $\pi_{C=O}$. The use of these values in Eq. (6) (see Fig. 11, the lower straight line), differently from aldehydes, ketones and a few other compounds, leads to a separate rectilinear dependence which is mixed approximately by 3 eV lower on the ordinate axis (IP($\pi_{C=O}$)). As it was mentioned, according to the previous interpretations, all amides will also lie on the same straight line,

Nevertheless, it can be said that using the interpretation of IP($\pi_{C=O}$) given in works[29,30,32] (the third orbital for HCOOH, the 4th for acetic acid, the third orbital for CF_3COOH) shows that in Fig. 11, these points move to the upper straight line, which coincides with that of aldehydes, ketones and of the above mentioned amides. Such an interpretation is also in keeping with the results of the data treatment by means of Eq. (6), the other compound series presented in Table 3. As another hypothesis, necessary to be proved yet, attention should be paid to the fact that applying on the basis of report[32] the arithmetic mean of IP from the 2nd and the 6th IP ((12.11 + 16.5)/2 = 14.4) for acetic acid, the arithmetic mean from the 2nd and the 6th IP ((11.9+ +15.8)/2=13.8) for CCl_2HCOOH, the arithmetic mean of the values of the 5th and the 6th IP for CHF_2COOEt ((15.6 + + 16.7)/2 =16.2) also result in the accumulation of the points in the region of the upper straight line in Fig. 11.

If the second IP for FCHO and F_2CO in the function of IP($\pi_{C=O}$) were replaced by the arithmetic means: for FCHO from 2a" and 1a" MO (16.5 eV) and for F_2CO from $2b_1(\pi_{C=O}, n_F)$ and $1b_1(n_F, \pi_{C=O})$ MO (17.9 eV), the points for these two compounds would also lie on the upper straight line in Fig. 11. This interpretation, however, contradicts the results of comparison of IP(π_{CO}) value of carbonyl-containing compounds

with the IP($\pi_{C=C}$) of alkenes and IP($\pi_{C\equiv C}$) of alkynes where the second band of the PE spectrum was used in the function of the π_{CO} orbitals for FCHO and F_2O.

The analysis of the effect of structure on the ionization potentials of carbonyl-containing compounds using both the "external" and the "internal" scales of substituent constants can be found in our earlier publications[2,5,36]. A possibility of quantitative description of the IP of carbonyl-containing compounds within the approach, taking into consideration the distribution of charge density (the Madelung potential) around the ionization center has also been discussed[37].

Concluding the surwey of the results of the analysis of the PE spectra of a number of carbonyl-containing compounds, it should be stressed that the problem definitely needs a further broader complex analysis, applying both quantum-chemical calculations as well as the methods of comparison and correlation analysis.

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C O N T E N T S

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